Vol.
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1952

VACUUM

A Review of Developments
in
Vacuum Research and Engineering

Vol. II JANUARY, 1952

TORPIDITY

THE RESPONSIBILITY of a surface barrier layer, or as Dr. Hickman calls it a torpid layer, for preventing the practical realisation of theoretical evaporation rates has been most strikingly and elegantly demonstrated by him in the course of investigations he has been carrying out for four years and a summary of which we are glad to present in this number.

Those appreciative of experimental skill will not fail to delight in the ingenious manner in which he has studied and recorded this important subject. We have taken particular care in reproducing for our readers the beautiful photographic studies which form such a unique part of Dr. Hickman's work, a technique which was seen by some of us in an even more impressive manner in the film which he used to illustrate his lecture on 'The Torpidity of Liquid Surfaces' during the Physical Society Exhibition (London) this year.

This conception of torpidity in the surface of boiling liquids is bound to stimulate ideas for practically improving evaporation rates and apart from the obvious field of distillation work, vacuum workers will wonder, to what extent the performance of diffusion pumps, dealt with from quite another aspect in this number, is influenced by this phenomenon.

DIFFUSION PUMP OILS

THE INVENTION of the diffusion pump some 40 years ago represented a contribution not so far surpassed in the production of high vacua. At the time of the invention only mercury was known to have the essential properties required for the operation of the diffusion pump but the now classic work of Burch some fifteen years later showed that diffusion pumps were capable of reaching considerably lower pressures when operated with certain oils which have a lower vapour pressure than mercury at room temperature. A great impetus to vacuum work followed upon this discovery.

Today a comparatively large variety of oil-like pump fluids are available to give the desired low pressure performance but their decomposition behaviour varies considerably, profoundly affecting in the first instance the performance of the pump and the conditions in the evacuated vessel afterwards.

We have now reached a stage therefore when, although the principles of vacuum pump design are becoming well understood, the continued development of the diffusion pump to meet the growing demands made upon it will significantly depend upon the contributions which the chemist can make in evolving fluids to meet the conflicting requirements of the ideal pump fluid.

Torkel Korling, U.S.A.

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Dr. Hickman was born in London (England), in 1896. He received his professional education at the Royal College of Science during the period of 1913-1925, at the end of which he took his degree. After the outbreak of World War I he interrupted his studies and joined the Smoke Corps organised by the Ministry of Munitions, where he served from 1916-1919.

Subsequently he joined the Eastman Kodak Laboratories in America, where he studied waste product recovery processes, an interest he has consistently maintained. Electrolytic cells which he designed have been installed in many motion picture laboratories for the recovery of silver. In 1938 he became Vice-President and Director of Research of Distillation Products Inc., a subsidiary company, now known as Distillation Products Industries, founded on his work on high vacuum distillation. Since 1948, he has divided his time between fundamental research on evaporation at Kodak and a private practice in vacuum technology.

Dr. Hickman's early process work led him to try conditioning packaged films in vacuum. From this he passed to the development of vacuum pumps—he is actually the inventor of the fractionating oil diffusion pump—and finally concentrated on vacuum stills. It was his centrifugal molecular still which enabled low-grade fish oils to provide Vitamin A concentrates for medicinal use. He also discovered a source of Vitamen E present in industrial waste.

Dr. Hickman's contribution to the development of vacuum distillation is of decisive influence on the progress of this technology. In recognition of the service he has rendered to science and technology he was awarded the John Price Wetherill Medal by the Franklin Institute in 1950.

Dr. Hickman has been granted 140 patents and has published more than 50 technical articles.

DONALD J. TREVOY, co-author of the article beginning on the opposite page, has been associated with Dr. Hickman's work at Eastman Kodak for the last three years. He was born in Saskatoon, Saskatchewan, Canada, in 1922. He is a Ph.D., and a Master of Science in Chemical Engineering.

EVAPORATION FROM LIQUID SURFACES IN VACUUM

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FOREWORD

This is a review of work which is being described at greater length in a series of six papers now appearing in *Industrial and Engineering Chemistry*, which cover researches made in Rochester during the past 4 years. In addition, there are a few new experiments and an introduction which launches the story with some frankly *post hoc* theorising. The key to the literature and our own papers will be found in the references.

Summary

THE BEST RATE at which a liquid *can* evaporate is generally unimportant at atmospheric pressures because distillation is conveniently done thousands of times more slowly. In the high vacuum still the optimum rate is the one that limits yield of distillate and thus assumes first importance. Previous investigations have suggested that *evaporation coefficients* ranging from 1-25 per cent. of those calculated by the Knudsen-Langmuir formula are common. Only mercury and carbon tetrachloride have shown coefficients of unity.

The authors' experiments were predicated on the theory that the liquids, irrespective of constitution, will show coefficient of unity from new, clean surfaces and that the same liquids in the state of out-of-the-bottle purity or less will show fractional coefficients. This proves to be the case.

The clean surface experiments were done with a falling-stream rate tensimeter, the soiled surface with various observation-post pot stills. When the equilibrium pressure is above 10 microns a soiled surface becomes SCHIZOID, divided into WORKING and TORPID areas. The working area has a coefficient near unity, the torpid two to one hundred times less. An expanding surface, as in a growing bubble, has a higher coefficient than a contracting surface, and more vapour is emitted behind a stirring paddle than in front. A technique has been devised for making exact measurements of vapour emission from stretched and pushed surfaces of known age and purity. As the surface reaches PRISTINE cleanliness, the evaporation coefficient becomes unity and does not diminish with later ageing of surface. Pristine surfaces are not ordinarily encountered, and proneness to superheat is an indication of the impaired permeability of a liquid's surface.

*M.S. received February, 1952

Sommaire

IL EST GENERALEMENT PEU IMPORTANT de connaître la plus grande vitesse à laquelle un liquide peut évaporer à pression atmosphérique, car la distlllation se fait convenablement à une allure mille fois moindre. Pour les alambics à vide, la vitesse optimum, est celle qui donne le meilleur rendement et qui prend donc la plus grande importance. Des études antérieures ont laissé apparaître, que des coéfficients d'évaporation allant de 1-25% de ceux calculés par la formule de Knudsen-Langmuir, étaient courants. Seuls, le mercure et le tétrachlorure de carbone avaient des coéfficients de 100%.

Les recherches de l'auteur partaient de la théorie, que des liquides, quelle que soit leur constitution, auraient des coéfficients unité, au départ de surfaces neuves et propres, tandis qu'ils n'auraient que des coéfficients inférieurs, au départ de leur flacon ou avec une pureté inférieure même. Ceci fut prouvé par l'expérience.

Les essais de surface propre furent faits avec un tensimètre, ceux des surfaces contaminées avec différents appareils à cuve munies de voyants. Quand la pression d'équilibre est supérieure à 10 μ, une surface contaminée devient chizoide, divisée en régions prolifiques et en régions torpides. La région prolifique a un coéfficient voisin de l'unité, la région torpide 2 à 100 fois moindre. Une surface grandissante, telle que dans une bulle en expansion, a un coéfficient supérieur à celui d'une surface en contraction, et plus de vapeur est produite derrière une palette d'agitateur, que devant. Une technique a été mise au point pour faire des mesures exactes d'émission de vapeur de surfaces tendues et contractées, d'âge et de pureté connus. Lorsque la surface atteint la pureté originale, le coéfficient devient unité et ne diminue pas ultérieurement avec le vieillisement de la surface. Les surfaces frèshes ne sont pas communes et la sensibilité à la surchauffe est une indication de la perméabilité réduite de la surface d'un liquide.

INTRODUCTION

THE ACT OF EVAPORATION, as it comes to our notice, is *net* evaporation, the excess of outgo over return of molecules from the surface of a liquid or solid to a gas. In a closed vessel under stationary conditions, gross evaporation is exactly balanced by condensation, net evaporation is zero, and the liquid is said to be in equilibrium with its vapour. In the high-vacuum molecular still, there is substantially no recondensation and *net* equals gross evaporation. Under most other circumstances, net evaporation is far less than gross, a familiar case being water, where the gross rate at normal boiling point is calculated to be 97.7 litres of liquid per square metre each second. No net rate approaching this phenomenal figure has ever been realised because of limitations of heat transfer. Even from the surface of a pond in a brisk drying breeze[1], the net rate rarely exceeds a ten thousandth of the gross.

The optimum rate of evaporation or condensation or both, *transvaporation*, can be calculated by the Knudsen-Langmuir equation[2],

$$W = 583.p.\sqrt{\frac{M^*}{T}}$$

and should evidently be equal to half of the two-way transport across an imaginary window[3], of the same area as the surface, situated anywhere within the saturated vapour. It is axiomatic that, if the gross rate of evaporation is *actually* less than this, the gross rate of condensation must be less by the same amount, otherwise the kinetic-thermodynamic books will not be balanced. For every molecule of liquid that 'ought' to pierce the surface but fails to do so, there must be a molecule of vapour that fails to enter, being reflected after an abortive strike. The departure from the optimum rate is of course well known as the *accommodation coefficient* of vacuum science. The reason why it is significant at low pressures is that gross evaporation diminishes a thousandfold, while it may be necessary to maintain high net evaporation in order to collect distillate. The factors limiting net evaporation, such as heat transfer and obstruction by external gas, become less and less significant with falling pressure until the accommodation coefficient, or rather, 'lack of surface permeability,' becomes the dominant factor.

We referred above to evaporation into a cross wind. A pond, a river, the ocean, or even the Dead Sea evaporate very similarly in similar winds and temperatures. The effect of dissolved salt is trifling compared with the resistance to escape through the atmosphere.

The situation would be far different on a lighter planet nearer the sun, where net evaporation into a rarer atmosphere would be much more rapid. Here, the river would evaporate faster than the pond and both would outstrip the sea, not because of the salt in the latter but from the scum of seaweed, driftwood, stranded fish, and dead sea gulls—all the flotsam and jetsam of the ocean—that would soon coat the surface with an impenetrable slime. At an imaginary starting time all three bodies of water would behave much alike but at some moment shortly afterwards the surface of the ocean would become obstructed and the great bulk of water potentially vaporisable would become imprisoned by a dynamically self-sealing coating. Another example would be a milk pudding. A bowl of milk placed in the oven forms a skin and ceases evaporating, while water evaporates smoothly to dryness. In an oven so cool that no skin forms, the milk and water both evaporate smoothly at roughly similar rates.

Suppose, on our light, warm planet, it were continually raining and the ocean were lashed with foam; the surface scum would not harden but would be redispersed in the sub-surface water. The self-obstruction phenomena, then, are evidently associated with quiet conditions of surface and non-return of vapour and, most importantly, with *impurities*, rather than with the overwhelming bulk of H_2O, $NaCl_2$, $MgCl_2$, and so forth that make up the ocean.

EVAPORATION AND ACCOMMODATION COEFFICIENTS

The argument applies with some aptness to the

*W = g/m²/sec, and p = mm. Hg.

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high-vacuum evaporation of liquids. We suggest that the conflicting measurements[4,5] and varied interpretations that are prevalent are a consequence of the *happenstances* at the surface. The accepted picture of an accommodation coefficient stems back to solids[6] with their relatively stationary surface mosaics and visualises a pattern ready to receive an incoming molecule. Liquids present a changing surface scene, far less connected with their basic chemistry than their purity and recent surface history. The coefficients differ according to whether one-way evaporation or condensation, or two-way transvaporation is in question. One-way condensation is no longer the mirror image of one-way evaporation but each is a (varying) step in a circuitous path of balance that corresponds *in toto* to equilibrium exchange. It is because of this that the departure of the experimentally measured rate of one-way evaporation from the calculated optimum is sometimes called the 'evaporation coefficient' instead of accommodation coefficient and we shall make the substitution in what follows.

Returning to the milk pudding analogy, it is evident that, if the oven were heated above the boiling point of water, the skin on the pudding would be disrupted to allow steam to escape, and the situation would (and, indeed, can often be seen to) stabilise with the skin pushed to one side while steam issues from a clear, open crater. The point to this analogy and the others cited previously is that analogous situations are met in high-vacuum evaporation.

The facts in support of these statements fall into two groups—common knowledge within the art, and certain experiments which we are about to describe. It is common experience that liquids 'bump' and fail to boil smoothly, particularly, in the vacuum pot-still. The surface, according to calculation, is transvaporating at a high rate, yet distillation or net evaporation does not occur. So resistant is the surface to emission of vapour that the liquid superheats and vapour, when it does come off, originates under relatively enormous pressure in a submerged bubble. Some reflection should convince us that the usual explanation of cooled surface layer and superheated bottom layer is inadequate to account for the phenomena ; super-heating is worst when the liquid is warmed gently in the thermostat. The problem resolves itself into the question, 'What quality does the main surface lack that the surface inside the bubble possesses?'

Again, measurements of net evaporation have been made by many workers on many fluids[7] during the past twenty-five years and, with the exception of Knudsen's experiments with *pure* mercury[8], the rates have all been far below optimum : 1 to 4 per cent. for water[9], 1 per cent. for glycerin[10], 25 per cent. for ethyl alcohol[10], and so forth ; and the measurements have disagreed *inter alia*. Some conclusions that can be drawn are:

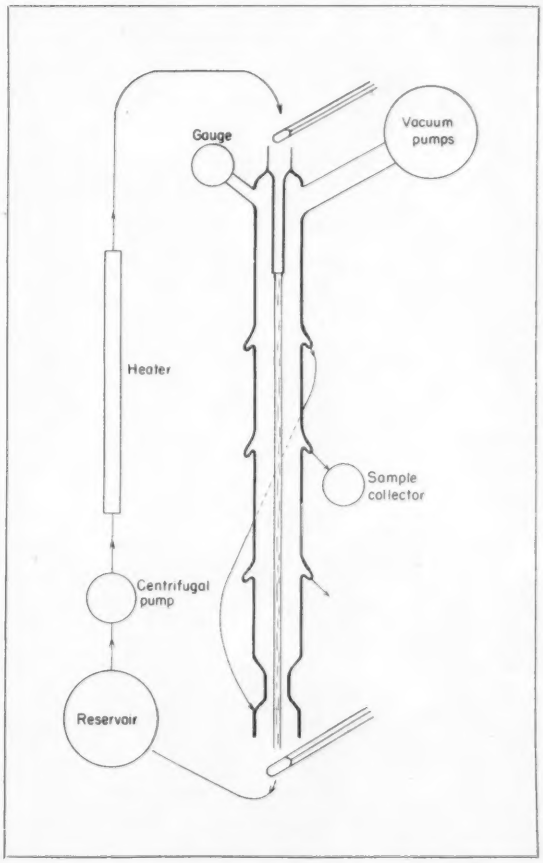

Fig. 1. Falling-stream tensimeter. Diagrammatic presentation.

(1) Most of the measurements were trustworthy but the interpretations were doubtful.
(2) Most of the low values were due to pot-still techniques. Evaporation was from a contaminated surface of ' ocean ' status.
(3) It can be predicted that perfectly clean liquid surfaces will evaporate at the calculated rate, at least if the rate be low. Net will equal gross rate and the evaporation coefficients will be unity.

SOME NEW MEASUREMENTS OF EVAPORATION

An experimental attack on the problem could best be waged on two fronts, the production and study of at least approximately clean surfaces and the study of the contaminated surfaces of everyday experience.

The technique we have used for the clean surfaces is the falling-stream molecular tensimeter[11] sketched in Figure 1. Samples of liquids, as chemically pure as we have been able to prepare, are circulated continuously through a reservoir and liquid jet system under high vacuum ($<10^{-3}$mm. Hg), while the quantity of distillate collecting in unit time from unit length of stream is measured. The evaporating surface is believed to be free from obstructive layers and is never more than 0.1 second old during the measured path. The three liquids critically examined, 2-ethylhexyl phthalate (EHP), 2-ethylhexyl sebacate (EHS), and glycerin, were found to evaporate at the predicted rates, indeed, to within 1 per cent. of theory at saturation pressures below 5 microns (about 3,000 complete molecular layers per second). At higher temperature, the rate falls off, as shown in Figure 2, presumably owing to the Fraser* cloud effect and to the instantaneous temperature-depletion gradients established in the surface. The rates still reach 75 per cent. of theory at the (commercially) tremendous rates of 60 grams per second per square metre, i.e., 216 kilograms per hour. Contrast this with rates 1/1000 of theory for glycerin and 1/2 to 1/20 for the same two pump fluids, exposed to high vacuum from beakers. Other measurements, which do not come into the main line of our argument since they involve relative volatility (α) of binary liquids, show that the *quality*, i.e. the α's, of equilibrium distillation and molecular distillation (completely non-equilibrium) are both the same[12] at rates below evaporation of 2,000 molecular layers per second, corresponding with 3 μ vapour pressure. At 50 μ, not more than 1 volume in 500 of the vapour transvaporating across unit surface in the equilibrium still can be withdrawn without disturbing the quality of the distillate. The point of importance, for our presentation, is that under suitable circumstances, all is well with the evaporation coefficient of a liquid —it is unity.

The dilemma with ordinary liquid surfaces is to know where to begin experimenting. A start[13] was made with the observation post shown in Figure 3. A 2-litre flask, attached to a cold trap, high-vacuum

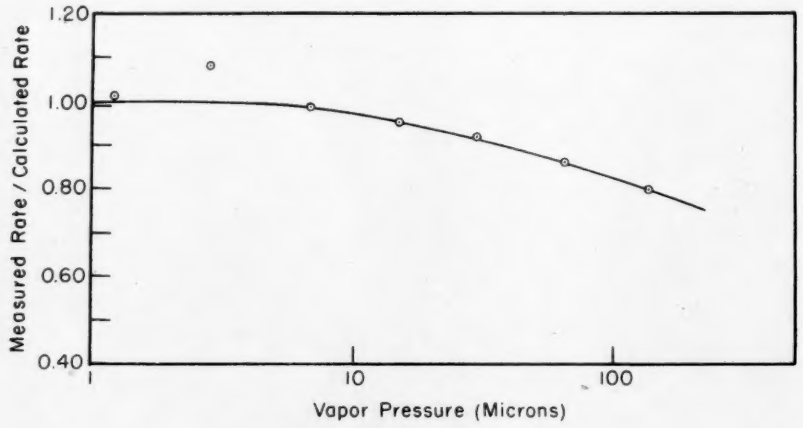

Fig. 2. Graph showing rate of distillation of 2-Ethylhexyl Phthalate as per cent of optimum rate.

*Private communication from R. G. Fraser concerning the self-obstruction encountered by a population of molecules diffusing from a crowded source into empty space.

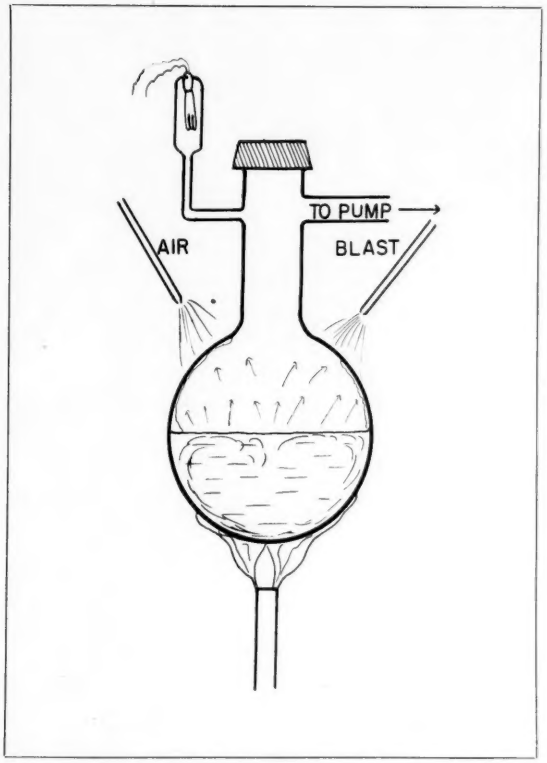

Fig. 4. Molecular pot-still under total reflux.

pumps, and a gauge, was mounted in front of a venetian-blind illuminator, presenting 1-cm. wide alternate black and white strips. This form of lighting allowed minute changes of surface texture to be seen and photographed. The flask could be heated with a Bunsen flame or an electrical jacket and could be lagged above or violently cooled, at will. The preferred combination was burner and air blast, as shown in Figure 4, which constituted a molecular pot-still under total reflux. For first observation, EHP (the vacuum-pump oil ' Octoil ') was a natural choice, since a considerable body of information is available concerning this liquid. Out-of-the-bottle ' pure ' commercial EHP was placed in the flask, vacuum induced, and gentle heating begun. After the first explosive degassing, the surface appeared entirely placid as in *a* of Figure 5, but as the vacuum grew better, $<1\mu$ and the temperature rose, the surface assumed an *active* habit, Figure 5*b*, and distillate streamed down the upper walls of the flask. The contents were kept at this temperature, about 140°C, equilibrium vapour pressure, 30 μ, overnight and the surface again examined. There now appeared a stagnant area to one side, marked off from the remainder by a very decided barrier which can be seen from above and below in photographs 5*c* and 5*d*. As the Bunsen burner was moved from the centre, the stagnant area moved sluggishly to the side *away* from the ascending stream. All very natural, one might reflect ; the cooler fluid collects away from the burner and shows less turbulence. But it turns out, from probings with a thermocouple, that the placid region is *hotter* than the turbulent and there is a sharp discontinuity between them. Also, when the placid region is more extensive, the pattern of condensate demonstrates that the placid area is emitting less vapour than the turbulent. It is, indeed, another *kind* of liquid surface, new to our notice. If either heating or cooling is diminished, the difference between the two areas alters and the junction may vanish. The phenomenon is produced by vigorous, one-way evaporation.

EXPERIMENTS WITH SCHIZOID SURFACE BEHAVIOUR

Suppose, now, that the observation flask be fitted with a dropping funnel for making additions and a still for withdrawing impurities—returning only purified distillate—continuously. Out of many substances tried at random, addition of 1 part in 10,000 of silicone pump fluid, or 1 in 1,000 of oxidised Vitamin A, or 1 per cent. of mineral oil (mechanical-pump oil) produced extraordinary differences between placid and active areas. An example with Vitamin A addition is shown in Figure 6. The phenomena are not confined to phlegmatic materials of high molecular weight ; witness allegedly pure butyl alcohol evaporating at −30° into a high vacuum, Figure 7.

FOOTNOTE: For Figs. 3, 5*a*-5*d*, 6 and 7 see pages 8, 9 and 10 respectively.

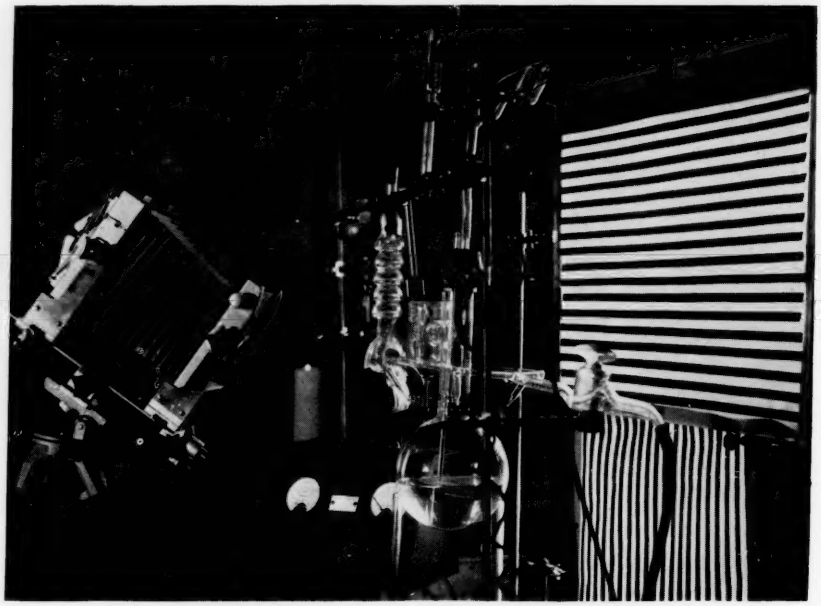

Fig. 3. Photographic assembly for examining evaporating liquid surfaces.

Fig. 5. (*a*) Cold EHP, showing placid surface.

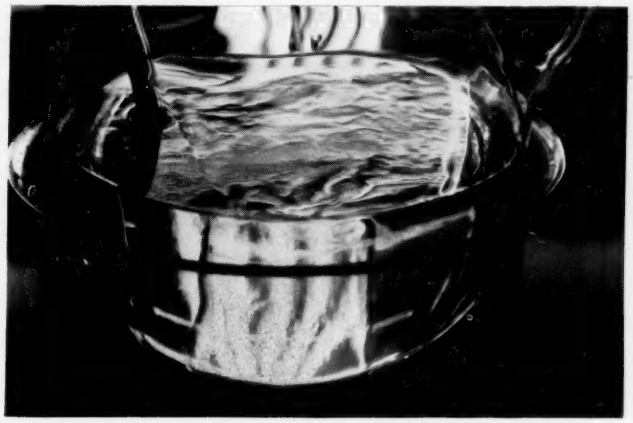

Fig. 5.
(*b*) Hot, evaporating EHP showing active surface.

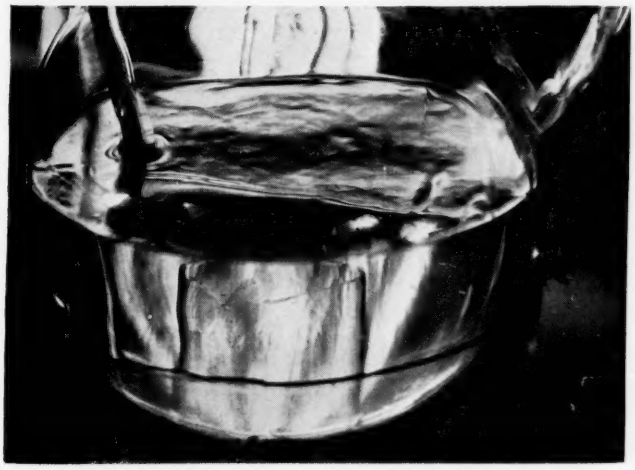

Fig. 5.
(*c*) Hot EHP, showing barrier between active and placid surfaces. —From above.

Fig. 5.
(*d*) Hot EHP, showing barrier between active and placid surfaces. —From below.

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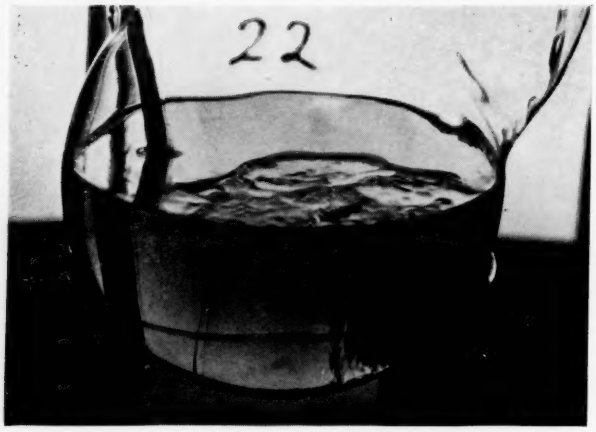

Fig. 6. ' Cast-iron ' torpidity, produced by adding oxidised Vitamin A to EHP.

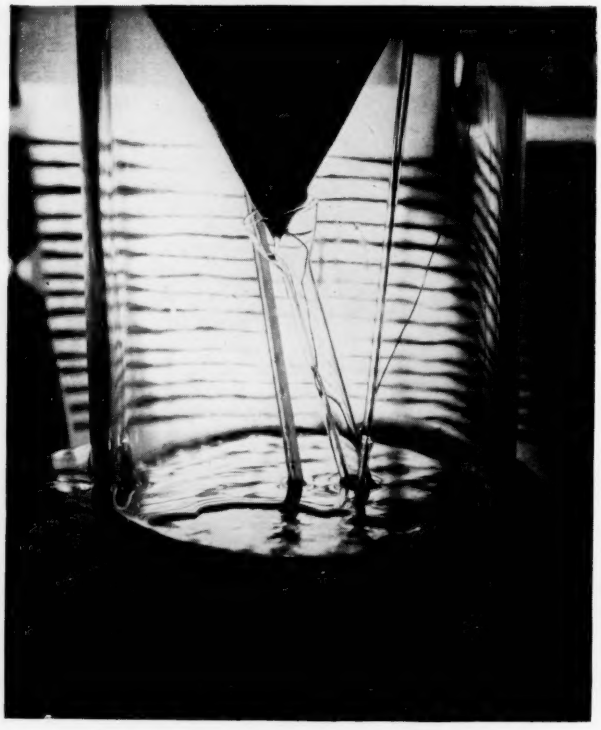

Fig. 7. Schizoid surface of *n*-Butyl Alcohol evaporating at −30° C.

When the purification still was put into operation, giving distillate sufficient for about four exponential dilutions a day, little change in the active-placid distribution occurred for about six weeks but by the eighth week, the barrier had vanished and the whole area of 2-ethylhexyl phthalate was highly active. As a preliminary guess, then, the placid non-evaporating areas are due to impurity, and extraordinarily little at that. The volumetric dilution in the eight weeks was of the order of 2^{224}, so that the elimination of non-volatile polymers should have been virtually complete. Reference to Figure 8 (see page 12) shows that the liquid in the flask was about 50 million molecules deep. One part in 100 million *could* produce an obstructive monolayer over half the surface if all became positioned there.

So, in imagination, we are able to watch the skin* of the molecular pudding being pushed by escaping vapour to one side of the dish. Could it not be pushed over the edge, if the dish were full? Two observation flasks were fastened together by an overflow weir and a simple system of valves and pumps was added to make the liquid overflow to the left or right, at will. Figure 9 shows three photographs *taken within* 5 *minutes*. The top one, with no overflowing, presents two SCHIZOID surfaces with TORPID and WORKING areas. Ninety seconds later, overflowing to the right has transferred the torpidity to the right, leaving a completely working surface on the left. The properties are permanent; cooling and reheating, with a week's interval in between, continue to reveal a torpid surface on the acceptor fluid, a freely working surface on the donor—*unless* new impurity of either *ex*- or *en*dogenous origin be acquired. The probable reason why the EHP in the earliest experiment was active at the start and schizoid later was that endogenous torpidogenic impurities had accumulated with time.

* The skin that limits rapid evaporation is a temporary or functional one and vanishes or re-dissolves completely when the cause is removed.

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Active and torpid, schizoid surfaces in both flasks.

Torpidity overflowed to right in 90 seconds, leaving active surface on left.

Torpidity transferred to left three minutes later.

Fig. 9. Double-flask assembly for overflowing torpid surfaces.

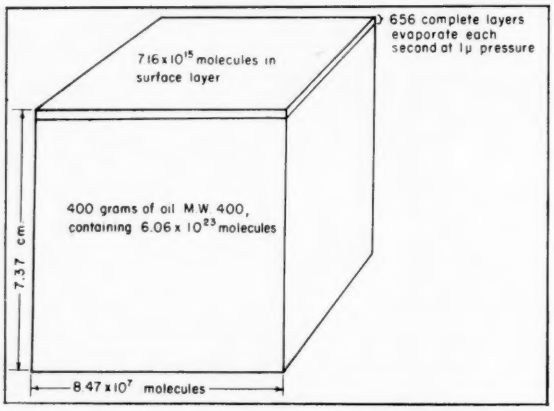
656 complete layers evaporate each second at 1μ pressure
7.16 x 10^15 molecules in surface layer
400 grams of oil M.W. 400, containing 6.06 x 10^23 molecules
7.37 cm
8.47 x 10^7 molecules

Fig. 8. Representing a gram-molecule cube of a typical vacuum-pump oil.

QUANTITATIVE MEASUREMENTS

To characterise the two surfaces further, at least two instruments were required : a probe to sample distillate (i.e., composition of vapour) and another probe to measure vapour emission from local areas. The first had already been produced[14] (Fig. 10, left) for other purposes and for the second, it was decided to construct a small anemometer with a dynamo on the shaft, supported by jewelled bearings (Fig. 10, right). This instrument, which will be discussed elsewhere, appears to have other uses in the vacuum field.

The probes demonstrated two basic facts. The torpid area has far less separating power (α of a binary mixture is lower) than an active, and the vapour emission is less by a factor of two to a thousand or more times. At lower temperatures when the schizoid pattern has not visibly developed, the emission of vapour is less than optimum for a pro-torpid liquid (and *all* liquids would seem to be potentially torpid unless the surface is specially prepared). The question now arises, what will happen to the vapour emission and α if we squeeze or stretch the evaporating surface? An experiment, simpler in design than execution, is indicated in Figure 11. EHP and EHS are circulated *in vacuo* over the obverse and reverse sides of two cones[15]. On the one, the surface is contracting ; on the other, it is expanding, see Table 1. At rates of evaporation less than 10 grams/sec/metre^2, α is significantly higher on the expanding side. We are thus in possession of the curious fact that the quality of vapour emitted by a mixed liquid under apparently ideal conditions of circulation in a closed system varies with minute changes in the manner of exposing the surface. When torpidity is present, as in an ordinary vacuum distilling-flask, we must conclude that the condensate is a composite of contributions varying in quality and quantity, according to the position of origin within the flask[15].

PUSH-AND-PULL SURFACE MEASUREMENTS

If α is affected by pushing or pulling the surface, so should the rate of evaporation be. As a corollary, less vapour should be emitted in front of a stirring paddle than behind it. Not only does this prove to be the case, but a simple set-up of stationary paddle and moving liquid furnishes a very convenient means for further *quantitative* study of high-vacuum evaporation of liquids. The procedure is indicated in Figures 12 and 13. The liquid is contained in an inverted bell jar and moved clockwise or the reverse by a magnetically coupled stirrer. A grid of submerged wire, controlled by a variable transformer warms the liquid, and vacuum is applied in the usual manner. A central core and paddle are lowered from the top plate and the anemometer gauge and thermocouple are lowered by a Trevoy shaft seal to any selected region near the barrier. 'Behind' and 'before' are thus determined by the direction of rotation of the liquid, while the degree of push or pull applied to the surface is varied by adjusting the rpm.

Now, competence in measurement is largely wasted unless one knows *what* one is measuring. In this case, there can be clean, overflowed surfaces of 'pure' liquids and at the other extreme, old surfaces of contaminated liquids. The latter are readily available, being furnished at once by almost any liquid poured into the apparatus ; the problem is to secure, maintain, and be sure that one has possession

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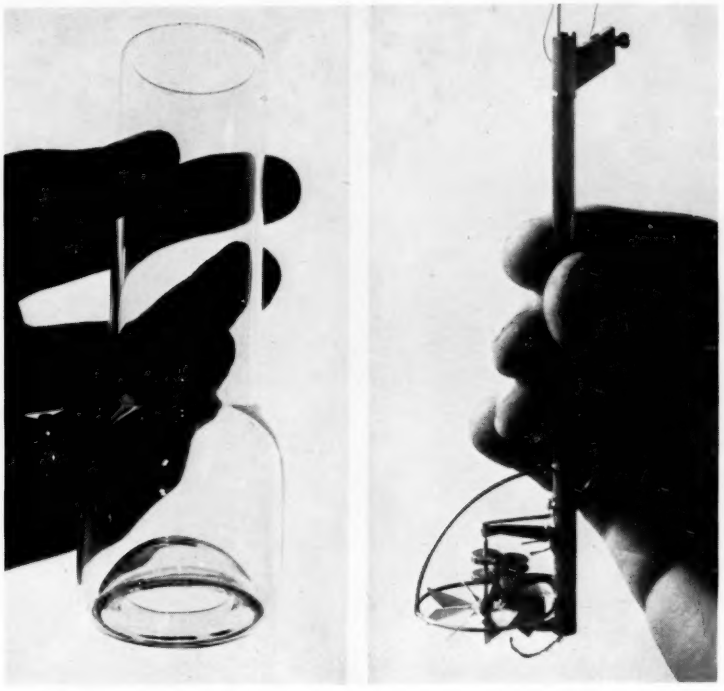

Fig. 10. Two high-vacuum probes. Left: Directional condenser. Right: Anemometer for registering vapour emission.

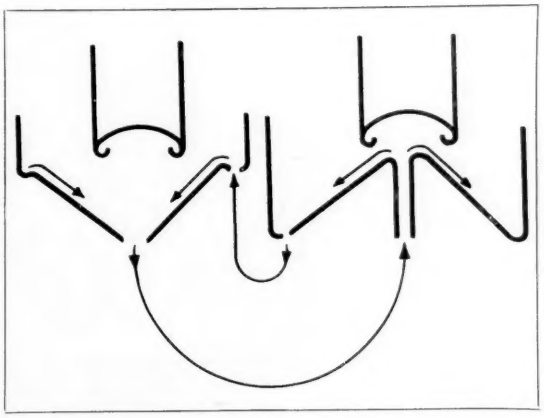

Fig. 11. Diagram of push-pull tensimeter.

Projective Distillation in Push-Pull Tensimeter

Temperature, C	Approximate vapor pressure	Relative Volatility	
		Contracting surface	Expanding surface
70	0.028	7.23	7.69
80	0.08	6.35	6.64
90	0.21	5.41	6.36
100	0.54	4.66	5.50
110	1.3	4.00	5.17
120	3.1	3.37	4.53
130	6.9	2.81	4.01

Table 1.

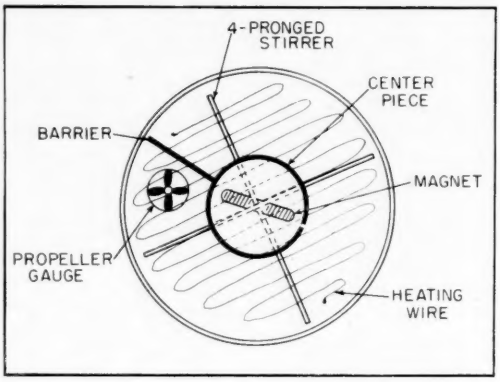

Fig. 12. Diagram corresponding to Fig. 13. A stationary paddle is half immersed in a liquid which is moved by a submerged paddle. The vacuum anemometer measures emission of vapour next to the paddle.

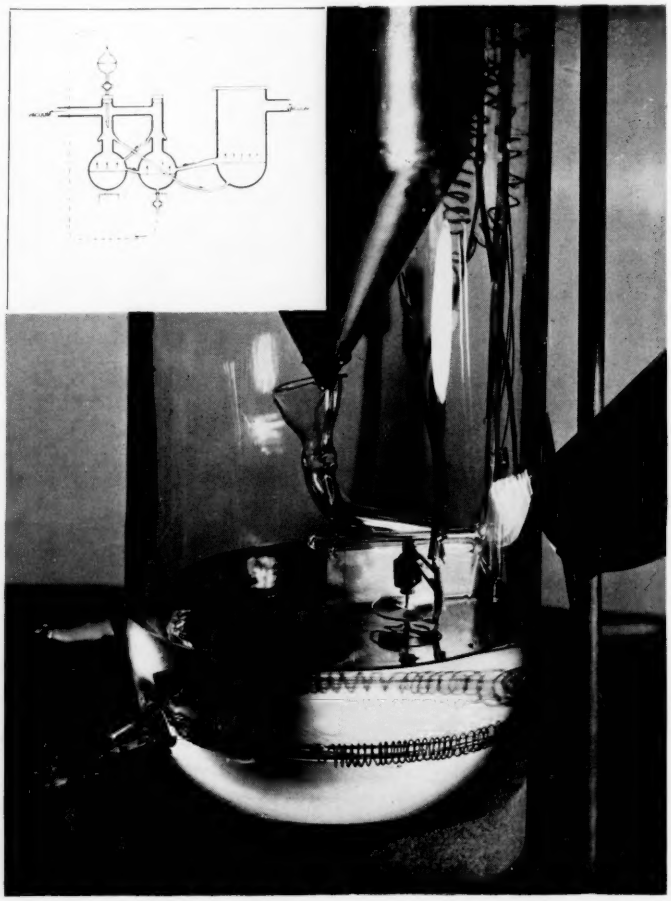

Fig. 13. Apparatus for quantitative measurement of vapour emitted by surfaces under different degrees of tension.

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of the former. It becomes imperative in the present case and, indeed, we believe, in all experiments of this type, to provide integral purification equipment that can be used at will or continuously. When pure surfaces are in question, the vessel must have the status neither of ocean nor pond but of a river or limpid mountain stream (definitely minus ' lusty trout or grayling '—in the molecular sense). The purification train of the stirrer experiment takes up most of the space in the photographs, Figure 13. The path of the fluids is shown in the left-hand corner. Torpid residues could be returned from the upper flask to the observation jar by way of the funnel fitted above the intermediate flask, thus enabling experiments with contaminants to be repeated.

There were six useful speeds on the reversing motor, varying from scarcely turning (5 rpm) to a turbulence only just short of splashing and drowning the anemometer. At any temperature, a series of readings could be made through the range : Push 8, 7, 6, 5, 4, 3, stop, pull 3, 4, 5, 6, 7, 8, or in the reverse order. Or, a direction and speed could be fixed while the temperature was raised or lowered. Evidently, a varied series of measurements can be made and the experiment, now six months old, is likely to be run for some considerable time before the available information will have been gathered[16]. However, some interesting conclusions can already be drawn :

(1) The difference between push-and-pull readings is inversely related to surface purity and projective vapour pressure. The purer the liquid and the lower the temperature, the less will be the difference.
(2) The repression of evaporation caused by pushing is due to two causes—bodily transfer of torpid areas to the approach side of the barrier, and compression of the now resident layer which may, or may not, have originated from the transfer.
(3) Measurements made through a cycle of stirring at constant temperature or through a cycle of temperatures at a constant force of push or pull result in hysteresis patterns that are reproducible.

The two sets of experiments that are presented here as typical involved EHP as representative of a single liquid and medicinal paraffin (Stanolind White Oil) as a complex mixture. Hysteresis curves for the former are shown in Figs. 14 and 15. As purification proceeds in the first case and as segregation of torpidogenic material advances in the second, the hysteresis patterns collapse and the vapour emission rises nearer and nearer to the optimum value, as determined by calculation and confirmed by the falling-stream experiments.

SOME CONSEQUENCES OF THE SCHIZOID SURFACE HABIT

We may now attempt some speculation concerning the formation of a torpid area on a fluid evaporating from a *flask*. Concerning the details, we have written at some length elsewhere[2,3] and will confine ourselves to the broader picture now. A working surface becomes started generally by hot striae of liquid, and evaporation proceeds apace, leaving torpid islands of stranded molecular flotsam. The working surface is driven downward and the torpid islands are driven laterally by vapour recoil. The islands coalesce to form the torpid area and the active area, now fed by liquid which has been largely freed from dissolved torpidogenisity, is able to ' work ' the more freely. The hydrostatic depression of the working area below the torpid area is caused by vapour recoil and is found to be equal to the *difference* of the two projective vapour pressures. Neither speculation nor experiment has yet revealed which of the two areas has the greater surface tension. From the data presented here and elsewhere we are emboldened to hazard the following generalisations[13] :

(1) Wherever there is a barrier between two phases, particularly between a liquid and its vapour at low pressures, the interface molecules will conspire to reduce traffic through the barrier to a minimum.
(2a) Wherever there is a difference of potential

FOOTNOTE: For Figs. 14 and 15 see page 17.

across the interface whereby mechanical work may be performed, the two phases will contrive *an engine* to *increase* traffic across the interface.

(2b) As a corollary, a highly contorted surface is evidence of the difficulty of facilitating traffic. The most actively working surfaces are the finest grained.

The synthetic mixtures which the organic chemist tries to distill represent probably the worst cases of torpidity, and the conditions employed are also the worst. Because a flask or pot-still has 'ocean' status, it is the sink and hold-all, from which nothing can escape surface-wise. All the dissolved impurities acquired from stoppers, grease, and attached columns become pushed into the evaporating surface. Steam distillation or the fine jet of air customarily employed to carry over the vapour now loom chiefly as devices for increasing and renewing surface area. Thus, the submerged and rapidly growing bubble now takes on the guise of Nature's foremost agent for producing a new, uncontaminated, expanding surface which can outperform as an evaporator anything the exposed and ancient top surface can offer.

Torpidity is a universally ubiquitous phenomenon in vacuum manipulation. The bumping of condensation pumps and their spasmodic action near the breakdown point is due to torpidity. Some pump oils superheat 40 to 60°C before an active crater will form and release vapour. The fluid then cools rapidly by evaporation, torpidity supervenes, and pumping action must wait for the next crater burst.

To the inevitable question as to whether torpidity extends beyond the 0.001—1.0 mm. Hg region just described, to higher and atmospheric pressures, where transvaporation is a thousand times greater, the answer is that we must wait and see what experiments reveal. There is already a *prima facie* case for accusing water of 'cast-iron' torpidity at its ordinary boiling point. And again, when we say water or other liquid is 'torpid', we should say 'prone to torpidity', because torpidity is not an intrinsic property but an artifact, a malady that afflicts their surfaces when contaminated. Many gross diluents do not confer torpidity; other trace contaminants cause severe infection.

We might have detoured in our researches to explore the chemistry of torpidogenic extracts or the effect of named additives; and of course this must soon be done. We should pose such questions as: Are they surface-active agents in the accepted sense? What is the effect on surface tension? But, since all the thirty or more liquids examined at random, from silicones evaporating at 250° to propane at −130° evaporating in the micronmillimetre range, show torpidity in a closed vessel and generally lose it when overflowed, we must conclude that it is a general, non-specific phenomenon caused by molecular flotsam under 'ocean' container conditions. Recent experiments are showing that the obstructive molecular layer arises often from the vapour phase. Torpidity can be caused by light as well as heavy impurities.

Perhaps in this omnibus presentation we have pictured surface obstruction as too haphazard an event. The semi-permeable layer will evidently have structure, the interstices of which must be larger than the evaporating molecules in those cases, where the rate of evaporation remains an appreciable fraction of the optimum. Structure implies intermolecular forces and it implies a selective concentration of molecules preferentially adapted to surface occupancy and cross linkage. Much theorising could be done but, while a little is already in order, we view the task chiefly as one of gathering more experimental information.

To the definite question implied in the preamble—'What is the evaporation coefficient of a liquid and how is it related to constitution?'—we can now reply, 'Constitution seems to be subordinate to the case history and present circumstances of the given sample. The coefficient becomes lower when there are dissolved impurities and when the surface is old.' In other words, the value can be anything from near zero to unity for any liquid.

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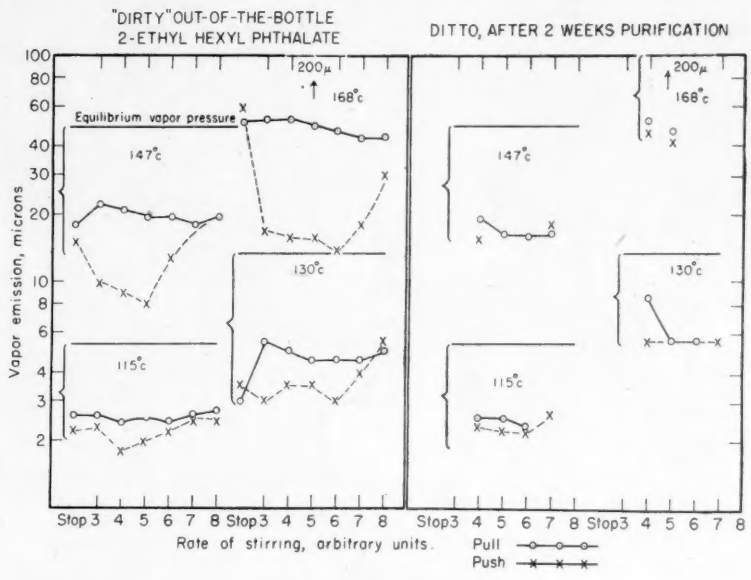

Fig. 14. Isothermal push-pull vapour emission curves. Hysteresis decreases as surface purity increases.

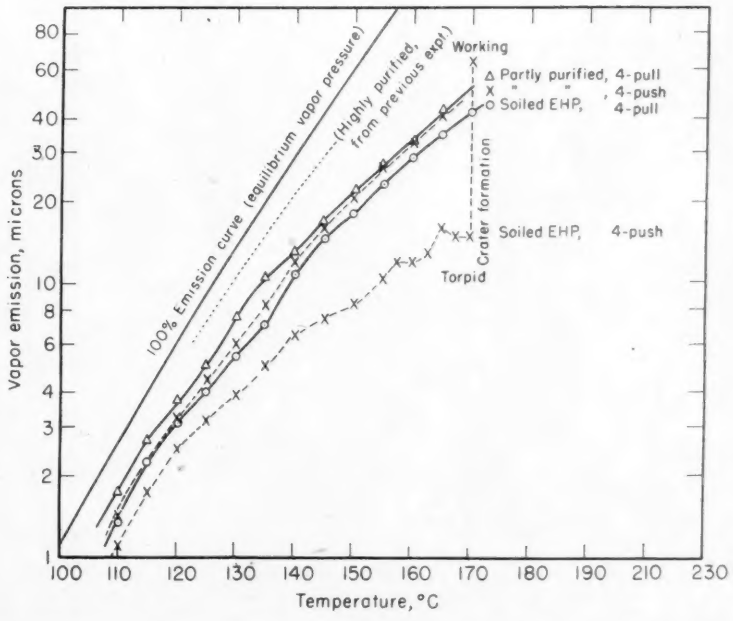

Fig. 15. Vapour emission–temperature curves for fixed values of tension of surface. Again, hysteresis decreases with increase in surface purity.

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APPLIED VACUUM METALLURGY

The Production of Magnesium, Calcium, Tantalum and Zirconium

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*Research Manager, Murex Ltd., Rainham, Essex**

Summary

THE USE OF VACUUM in the production of specific metals on an industrial scale is described. Details of the processes used for the production and treatment of magnesium, calcium, tantalum and zirconium are given. The work described indicates that the improvements in vacuum equipment together with the experience which has been gained by metallurgical engineers will lead to a rapid development of vacuum metallurgical techniques.

Sommaire

DESCRIPTION DE L'EMPLOI du vide à l'échelle industrielle pour des métaux spécifiques. Détails des procédés utilisés pour la production et le traîtement du magnésium, du calcium, du tantale et du zircon. Le travail décrit indique, que les progrés réalisés daus les appareillages à vide, joints à l'expérience acquise par les ingénieurs métallurgistes, conduiront à un développement rapide de la technique métallurgique à vide.

INTRODUCTION

THE USE OF VACUUM METHODS in metallurgy has increased considerably in recent years. Dr. Kroll in an article published in the July 1951 issue of this journal examines the characteristics and the scope of these methods and gives an impressive account of their importance to metallurgy as a whole. He mentions a great number of vacuum processes which can today be considered as being established and forecasts future penetration of many branches of metallurgy not yet effected by existing methods.

The author of this article proposes to give a detailed account of four of the leading processes in metal production where the provision of a vacuum at certain stages is an essential feature of their success.

Magnesium is the outstanding example of vacuum metallurgy because although it was produced by methods other than those requiring operations in vacuum, its large scale vacuum production was almost spectacular.

The process for magnesium production which obtained the greatest prominence was known as the Pidgeon Process and was based on the thermal reduction of calcined dolomite with ferro-silicon. In actual fact magnesium was produced by thermal reduction in apparatus similar to that used by Pidgeon, many years before his process was operated. In particular, a commercial plant was operated in the United Kingdom as early as 1935, in which magnesium was produced by heating a mixture of calcined magnesite with calcium carbide in steel retorts which were maintained at a low pressure by means of mechanical vacuum pumps.

The shortage of magnesium in the last war created an emergency which undoubtedly was solved largely by the ferro-silicon process. Little was known at that time about large scale vacuum engineering but very soon the necessary plant was assembled and operated

*M.S. received November, 1951

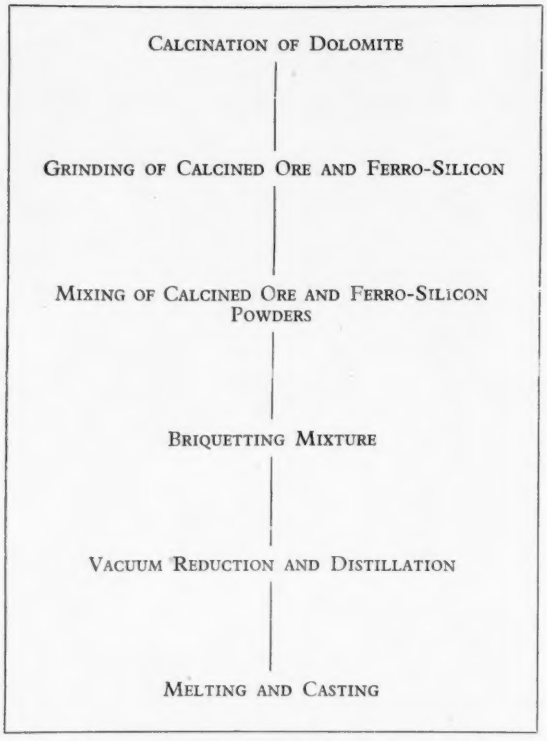
Calcination of Dolomite
Grinding of Calcined Ore and Ferro-Silicon
Mixing of Calcined Ore and Ferro-Silicon Powders
Briquetting Mixture
Vacuum Reduction and Distillation
Melting and Casting

Fig. 1. Flow Sheet of the ferro-silicon magnesium process.

successfully to produce thousands of pounds of metal per day at pressures as low as one micron. The success of the process demonstrated that it was possible to operate large vacuum plants economically.

FERRO-SILICON OR PIDGEON PROCESS FOR MAGNESIUM

The ferro-silicon process required to be operated in vacuum for two reasons : firstly, to lower the temperature at which the metal could be distilled after reduction, and secondly, the reduction operation had to be carried out in the absence of air because of the activity shown by magnesium towards the common gases at elevated temperatures.

The reaction which occurs when dolomite is heated with ferro-silicon is a simple reduction of the magnesium oxide by the silicon, the lime which is present in the dolomite combining with the silica formed during the reduction and producing calcium silicate. The direct use of dolomite with no treatment except calcination was a definite advance over the older processes using magnesia, because although calcined magnesite was used supplies of this material were difficult to obtain and there were large natural sources of dolomite in many countries. Ferro-silicon possessed advantages over both the other reducing agents, calcium carbide and aluminium. For example, it could be readily and safely comminuted whereas aluminium must be atomised and calcium carbide crushed and handled in a dry inert atmosphere to avoid the production of the explosive acetylene.

In order to obtain the intimate contact, necessary in solid/solid reactions, the dolomite and ferro-silicon were finely ground and briquetted. The pellets were charged into horizontal alloy-steel retorts which were maintained continuously at the reaction temperature. After charging, the open end of the retort was sealed and the retort evacuated. After the charge attained the reaction temperature the magnesium distilled and collected in a condenser on the cooled discharge end. The retort was opened while at temperature and the magnesium crystals removed, followed by removal of the residue which being mainly di-calcium silicate did not sinter or slag.

The operating pressure was below 0.2 mm. Hg or 200 microns Hg ; this was considerably lower than required for the removal of the metal from the briquettes but it ensured that the metal was not contaminated with oxide or nitride. Whilst good yields were obtained up to 500 microns Hg, there were indications that the plants operating at the lower pressures showed the lowest melting losses, indicative of the purity of the crystals.

It has been reported that the effect of operating at pressures above 500 microns Hg was very obvious, the crystals being badly contaminated with oxide, nitride and a blackish pyrophoric dust. In addition to the decrease in purity of the crystals there was the possibility that the pyrophoric metal may be ignited by the sodium and potassium produced during the reaction, bursting into flame when the retort was

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opened. The dense metallic crown formed at lower pressures did not ignite readily.

As the retorts were maintained at full temperature the charge attained reduction temperatures, about 1,170°C., in a very short period. It was essential for successful operation of the process that the vacuum pumps should have produced the desired low pressure within the retort before the reduction temperature was attained. During heating large volumes of gases were evolved and the pumping capacity had to be such that a pressure in the region of 100 microns Hg or lower could be obtained in a period of less than one hour. A high speed continuous vacuum system was used to cope not only with the evolved gases but to deal with leaks, and the outgassing of metal parts. Therefore, the pumping had to deal with two stages : firstly, evacuating large volumes of gas produced at a relatively high pressure and secondly, maintaining a low pressure for the remainder of the cycle, which was about 7-8 hours.

The following types of pumping equipment were available to produce the desired requirements, (*a*) rotary oil-sealed mechanical vacuum pumps, (*b*) multistage steam jet ejectors, and (*c*) diffusion pumps in combination with suitable backing pumps. The mechanical pumps were available in sizes ranging from 25 to 600 cubic feet per minute capacity. Steam jet ejectors had not had many applications at pressures in the micron range and because of their large size, complex systems would have had to be evolved to make them suitable for operation on plants using large numbers of small retorts.

No large diffusion pumps were available that combined high pumping speed in the range 1 to 500 microns Hg with the ability to operate against high fore pressures. However, during the construction of the magnesium plants, diffusion pumps using both oil and mercury vapour, were developed for the process. These pumps were capable of handling extremely large gas volumes at pressures below 1 mm. Hg, and were operated in combination with rotary mechanical pumps.

Steam jet ejectors were successfully operated in one plant using very large retorts.

Experience indicated that there was probably a place for all three types of pumps which have been mentioned. The steam ejector was suitable for handling extremely large quantities of gas at moderate pressures, while the mechanical pump was useful over the entire range of pressures involved in the ferro-silicon process. Diffusion pumps were particularly suitable for the lower pressure ranges.

In the case of the steam jet ejector, clogging of a jet or a breakdown in the steam supply could cause an immediate rise in pressure with the possibility of steam or water being forced into the hot retorts. This disadvantage could be overcome by automatic safety devices but nevertheless many designers avoided the use of this type of pump.

The successful operation of the mechanical pumps depended mainly on the avoidance of contamination of the oil. As water vapour is liberated from the charge it was necessary to ensure that there was a continuous flow of purified and dried oil to the pumps. The cost of providing the pumps with clean oil was considerable, and elaborate oil purification systems were developed.

For operating pressures in the region of 100 microns Hg or lower the diffusion pump was the most economical means of vacuum pumping.

One of the pumping arrangements which proved simple and efficient to operate with the ferro-silicon process was evolved from a combination of mechanical and diffusion pumps. The mechanical pumps were used to evacuate the retorts, and at the end of this roughing cycle the system was turned over to the diffusion pumps which rapidly completed the evacuation and maintained a low pressure during the remainder of the cycle.

In addition to the problem of producing a satisfactory vacuum in the ferro-silicon magnesium process there was the problem of measuring it. In general, only two pressure indicating instruments were used, McLeod gauges of the tilting type, and thermocouple gauges. The former is an absolute instrument in which calibration is made from the dimensions of the gauge itself, whereas the thermocouple must be calibrated against a standard.

The principle of the McLeod gauge is well known, its limiting factor being caused by the fact that the

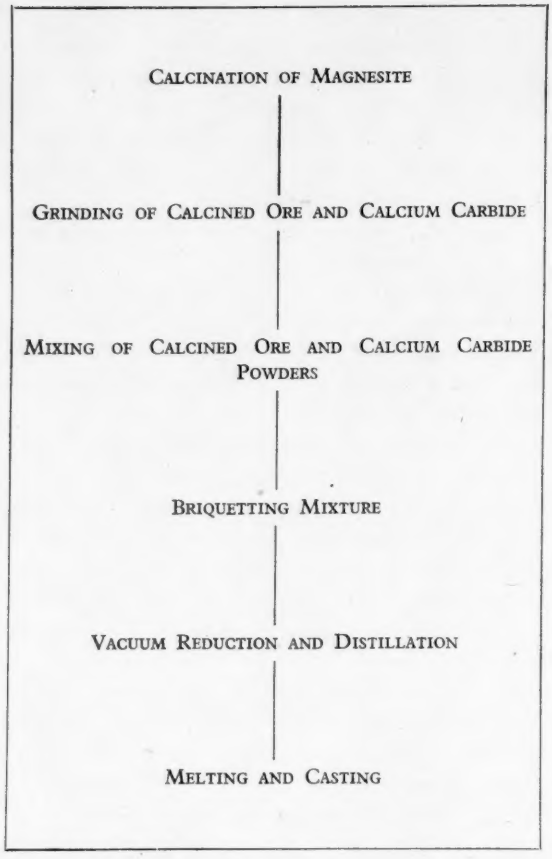
Calcination of Magnesite
Grinding of Calcined Ore and Calcium Carbide
Mixing of Calcined Ore and Calcium Carbide Powders
Briquetting Mixture
Vacuum Reduction and Distillation
Melting and Casting

Fig. 2. Flow Sheet of the calcium-carbide magnesium process.

gas is compressed to measure the pressure and, therefore, the instrument does not accurately indicate the partial pressure of condensable vapours such as water, and it is essential to use a cold trap to remove condensable vapours, if accurate readings of permanent-gas pressure are to be obtained.

The thermocouple gauge was much more expensive than the McLeod gauge but cost is relatively unimportant in the production of essential war material. The gauges were connected directly on to the piping and continuous pressure records could be obtained which assisted greatly in the control of operations which were continuous. Some trouble was caused by failure to appreciate the importance of small leaks due to imperfect fitting of the gauge into the system.

During construction all new piping systems were subjected to an initial ' soap and bubble ' test and a final test under vacuum. Where thermocouple gauges were used vacuum leaks could be detected by spraying the suspected point with acetone or other volatile liquid.

CALCIUM CARBIDE MAGNESIUM PROCESS

The data given above relates to the production of magnesium in America and although, as stated previously, the metal was produced in England by Murex Ltd. at an earlier date, no information has been published on these operations. The plant was shut down before the end of the last war when the enormous production capacity of America got under way.

It is interesting to compare the process as carried out at Murex with the reports on the American work, and, in particular, to note the difference in working pressure.

According to the published information it should not have been possible to obtain good metal at the pressures used in the Murex plant whereas good yields of excellent metal were actually obtained. The low pressures reported in the literature dealing with the Pidgeon process may be misleading as there is no indication of the location of the point at which the pressure was measured. In fact, if the low pressures quoted were obtained in the retorts, it is rather odd that the operators did not find difficulties arising from the high volatility of the chromium present in the alloy-steel retort.

The Murex process was based on the reduction of calcined magnesite with calcium carbide ; a small amount of fluorspar was found to improve the yield and an addition of this mineral was always made. The magnesite was calcined in a rotary kiln and ball-milled to pass a 200-mesh sieve. The processing of the calcium carbide was complicated by the explosive hazard and it was necessary to crush and mix in a dry inert atmosphere. The necessary condition was produced by burning coke under regulated conditions

to produce a gas which was largely carbon dioxide, subsequently dried by passing through silica gel units before entering the system. Although the drying arrangements were not ideal no serious explosion occurred during the whole ten years of operation. The milled carbide and magnesite, and a little fine fluorspar were mixed in a sealed container. A typical mix was as follows :—

100 lbs. calcined magnesite (89% MgO)
188 „ calcium carbide (83.2% CaC_2)
10 „ fluorspar

The mixed powder was fed to hoppers and hence to a battery of single-acting briquetting machines, where briquettes 2¼ inches diameter and 1 inch thick were pressed at a total pressure of 30 tons. The briquettes were fed continuously to containers which were lowered into the retorts and withdrawn leaving the charge ready for treatment.

The retorts which had one end closed, were forged from carbon steel. The inner diameter of the retorts was 14 inches and the overall length 14 ft. 6 ins. of which about 2 ft. projected from the top of the furnace. The open end of the retort was closed with a steel lid forming a spigot and socket joint on the tube end. The most satisfactory jointing material was found to be 10 gauge lead wire, although occasionally this caused trouble due to attack from the alkali metal produced during processing. After sealing, the retorts were lowered vertically into a furnace heated with producer gas. The carbon steel retort was protected by means of a heat-resisting sheath fitted on the outside of the retort. The retorts were heated to a temperature of 1,120-1,140°C. as measured by thermocouples within the furnace.

The 12 retorts were connected to a ring main made up from three-inch pipe, all joints being made with rubber gaskets. The valves used were Newman Milliken standard grease-lubricated plug-type ; high temperature grease and not vacuum grease was used. Connections between the three-inch manifold and the retorts were by one-and-half-inch pipes, and between the manifold and pumps three-inch pipes were used. The manifold was sub-divided by valves so that a group of four retorts were connected to one pump. Mechanical pumps only were used, these

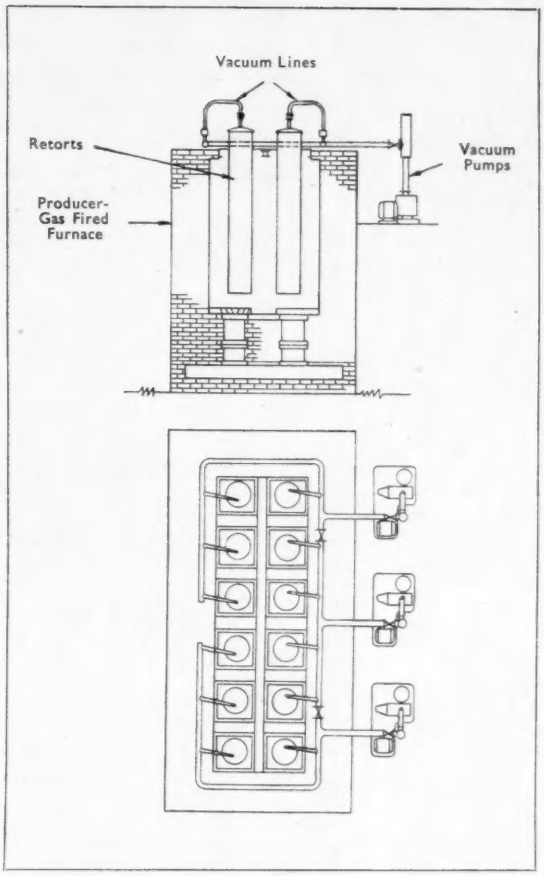

Fig. 3. Vacuum system on the Murex magnesium process.

being the rotary type, powered by 5h.p. motors, and each capable of pumping 110 cubic feet per minute at atmospheric pressure. Although an oil purification installation was often contemplated, it was never installed and the usual practice was to run the pump for 14 days, when the old oil was drained and fresh oil added.

In view of the moisture and dust that were picked up by the oil, it is surprising the systems continued to operate. However, despite the dust the pumps showed very little signs of wear after several years of almost continuous operation.

The pressure was measured by a simple barometer-type gauge and a good vacuum was about ½ to 1 mm.

Hg, obtained after pumping off very large volumes of gas evolved during the preliminary stages. The gauge was fitted in the system about 5 feet from the pump and about 8 to 9 feet from the retort. About 8 hours was required to raise the charge to temperature, by which time the pressure had steadied to about 1 mm. Hg.

In the later stages of operation considerable improvement was obtained by the use of a two-inch pipe inserted vertically in the middle of the charge. The pipe which had numerous one-inch holes throughout its length facilitated the passage of the metal vapour.

The metal vapour distilled to the top of the retort, where it collected on a split-tube steel condenser. The top of the retort was cooled by a stream of air directed on to it by a large fan ; this was found necessary only after the building had been ' blacked-out ' when natural ventilation was considerably reduced. The whole heating cycle was 24 hours, on the completion of which the 12 retorts were lifted out of the furnace and allowed to cool for 12 hours before removing the cover.

Solid crowns of metal with some adhering dust were lifted out attached to the condensers and after separating, the crowns were melted in steel crucibles with suitable flux composed of a 50/50 mixture of magnesium chloride and fluoride, and by agitation it was found possible to produce a bath of clean metal which was cast continuously into slabs. Sulphur was dusted over the surface of the metal during pouring to produce a protective atmosphere of sulphur dioxide. Melting and casting under vacuum had been investigated but it was found possible, by the use of a special pouring lip on the crucible, to produce a condition, whereby the metal could be poured without oxidation.

The retorts were charged with about 550 pounds of mixture and yielded 70 to 80 pounds of metal. The average recovery was about 80 per cent. The loss on melting to ingot was small, less than 5 per cent. The purity of the metal was generally of the order of 99.9 per cent.

It is obvious that the details given above of the operation of the Murex process are not a recommendation for this type of plant, but rather an attempt to indicate that even under adverse conditions, large scale vacuum operations can be relatively successful. Maintenance costs were high and it was probably a mistake to use such large retorts, as the time required for the heat to penetrate the charge was excessive.

Pidgeon's scheme for maintaining the retort continuously at reaction temperature resulted in considerable saving of time and gas. The retorts at Murex, like Pidgeon's, lost their shape and required to be reforged. The heat resisting sheath was not entirely satisfactory due to the difficulties in obtaining an airtight joint, and probably did nothing more than protect the retort from flame impingement.

CALCIUM PRODUCTION

The production of calcium by thermal reduction in vacuum is interesting because, like magnesium, it was a war-time development which resulted in an improved vacuum technique.

Metallic calcium has been produced for some time by the electrolytic process but during the war large quantities of calcium were required urgently and as it was difficult to expand the electrolytic plant in a reasonable time, it was decided to investigate a thermal reduction process which could be operated in the New England Lime Co.'s magnesium plant which had idle capacity. The process operated was very similar to that used for the production of metallic magnesium, and consisted in the reduction of calcium oxide with aluminium. Operations in vacuum were, as in the case of magnesium, required for two reasons : lowering of the boiling point of the metal and protection of the active metal vapour and solid from the atmosphere. It was impossible to use silicon as in the magnesium process, as the temperature required for this reaction exceeded 1,200 °C. which was the maximum operating temperature of the alloy steel retorts. Tests indicated that aluminium would be satisfactory at temperatures from 1,170 °C. to 1,200 °C. As in the case of magnesium the vacuum served a two-fold purpose, to reduce the temperature required in order to distill the metal and to avoid oxidation by the atmosphere.

As the calcium metal was required for the production of calcium hydride which could be used as a source of hydrogen, purity was not very important. Nevertheless, it was necessary to use high grade limestone as a starting material, since any magnesium, barium, strontium, sodium and potassium which might be present would be reduced and distill over. The alkali metals, potassium and sodium, were particularly objectionable as they often ignited on exposure to the atmosphere.

The limestone was calcined in a rotary kiln to produce calcium oxide which was milled to a fine powder.

The aluminium used for the reduction was the fine powder collected in the filter bags during the production of atomised metal. The aluminium content was from 96 per cent. to 99 per cent. It was desirable to use aluminium free from volatile metal such as zinc and magnesium but other high boiling metals such as iron and copper did not interfere.

The aluminium powder and lime were mixed and briquetted without a binder in a roll-type press into ovoid briquettes.

The retorts which were used in the process were the same as for magnesium. They were formed from a 28 per cent. chromium, 15 per cent. nickel alloy and although they tended to collapse after a time it was found possible, by applying a pressure of 100 lbs. per sq. in. at the top temperature, to blow the retorts into shape again. This operation could be repeated many times before the retort finally failed.

The retorts were placed horizontally in a producer-gas fired furnace with about two feet protruding from the furnace. The last foot length was jacketted and water-cooled to condense the metal vapours and protect the rubber gasket fastened on the cover which was used to obtain the vacuum seat.

The briquettes of lime and aluminium were charged into the hot retorts in paper bags, and a length of pipe which acted as a condenser was inserted in the cooled end of the retort.

The covers were placed in position, after the paper bags had burned, and sealed by the application of the roughing vacuum obtained by mechanical pumps. The roughing was continued for about an hour when

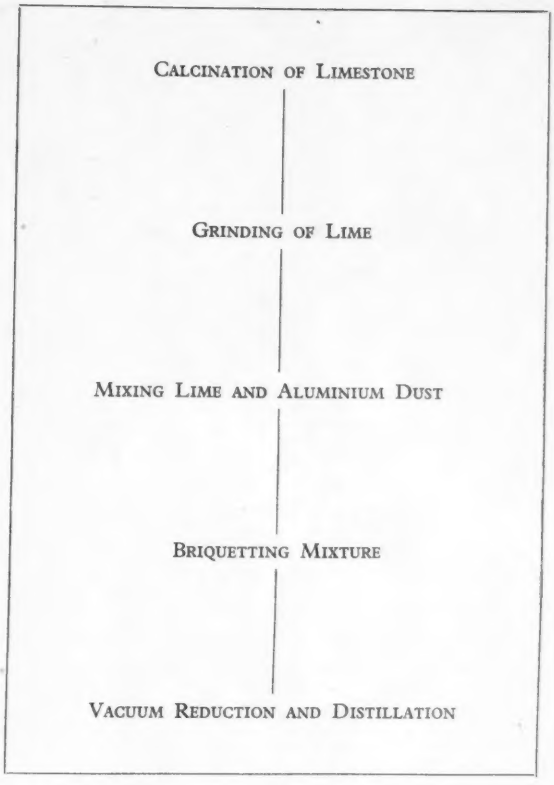

Fig. 4. Flow Sheet of the calcium production process.

the pressure, as measured by a McLeod gauge, was about 500 microns Hg. At this stage the retorts were connected to the high vacuum system. The system used was to run mercury diffusion pumps backed by mechanical pumps. The mercury diffusion pumps were used in groups of five to service a furnace of twenty retorts. The mechanical pumps, each of which had a capacity of 100 cubic feet per minute, only operated successfully when supplied continuously with purified oil. Purification was achieved by heating the oil in vacuum and filtering it before returning to the pumping system.

Details of the diffusion pumps are not reported but within an hour of switching the high vacuum pumping unit into the circuit, the pressure dropped to 20 microns Hg or less.

The high vacuum was measured and recorded by

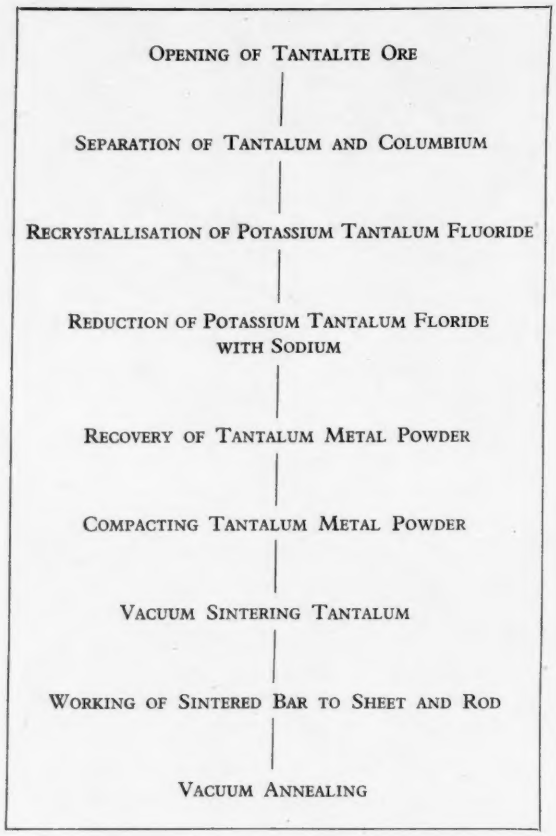
Opening of Tantalite Ore
Separation of Tantalum and Columbium
Recrystallisation of Potassium Tantalum Fluoride
Reduction of Potassium Tantalum Floride with Sodium
Recovery of Tantalum Metal Powder
Compacting Tantalum Metal Powder
Vacuum Sintering Tantalum
Working of Sintered Bar to Sheet and Rod
Vacuum Annealing

Fig. 5. Flow Sheet of the tantalum production process.

equipment actuated by thermocouple gauges. As in the case of the ferro-silico magnesium process, there is no indication of the position of the gauge in the system.

The calcium vapour condensed on the steel pipe as a dense tough mass of large crystals slightly contaminated on the surface with oxide and nitride. The principal impurity was magnesium, and this varied from 0.5 to 2 per cent. Aluminium was a maximum at 0.2 per cent. with manganese from 0.005 to 0.02 per cent. The nitrogen was under 0.02 per cent. No suitable method for determination of oxygen was available.

It has been reported that calcium made by the thermal reduction process could not compete successfully in the United States against the electrolytic product, but as the thermal metal appears to have been of high quality it is difficult to understand this statement as it would be expected that the large scale production could be more cheaply achieved by the thermal technique.

TANTALUM AND ZIRCONIUM

The three metals tantalum, zirconium, and titanium, like magnesium and calcium, are extremely reactive towards the common gases at moderately elevated temperatures and their successful production is best achieved by the use of vacuum techniques. In the case of tantalum the work goes back some time, while the production of zirconium and titanium is comparatively new.

Tantalum as ductile metal was first produced at Siemens & Halske, Berlin, in 1903. The first part of the process, the opening of the ore and separation of the tantalum from columbium which is always present in tantalite and other tantalum minerals, is interesting but beyond the limits of this paper. The second part of the process is the production of tantalum metal in the form of powder. The tantalum is recovered from the chemical plant as pure dry crystals of potassium tantalum fluoride and the next step is to convert this to tantalum metal. Von Bolton used sodium to reduce the double fluoride and later Balke of The Fansteel Company of U.S.A. developed an electrolytic process. Although the electrolytic process appears to be satisfactory the Siemens reduction method is very simple and produces fine soft powder which is excellent for pressing to bars for further treatment. It is not necessary to carry out the reduction of the potassium tantalum fluoride with sodium in vacuum as an excess of reducing metal is present, and thus the metal vapour provides a protective atmosphere. The reduction is carried out in steel pots, closed with a weighted lid and, provided care is taken in mixing the charge, excellent results can be obtained. The salts produced during the reduction, *i.e.* sodium and potassium fluorides, are leached from the reduced mass and the tantalum powder is recovered.

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The final stage in the production of tantalum is conversion of the powder to solid metal which may be fabricated to sheet and other useful forms. As this entails heating a pressed bar to a temperature in the region of 2,500°C. it is necessary to carry out this operation in a high vacuum to avoid contamination by the common gases. The sintering technique employed at Siemens & Halske was rather involved and included three sintering stages, all of which occupied a considerable time. It has been proved possible to eliminate the first two pre-sintering stages and to sinter in one operation by passing current through the bar provided arrangements are made to cope with the shrinkage. The bar is supported between suitable clamp electrodes and surrounded by metal baffles to reduce the heat loss from the heated bar. The vessel is sealed using water cooled rubber gaskets. The pumping system used at Siemens has not been described in detail but it appeared to be composed of a small mechanical pump backing a very small mercury diffusion pump such as is used for evacuating electronic tubes. The furnace was first evacuated to a pressure of 0.001 mm. Hg but as soon as heating commenced the pressure rose due to the evolved gases. The pressure attained at full temperature in the final stage was 0.02 mm. Hg.

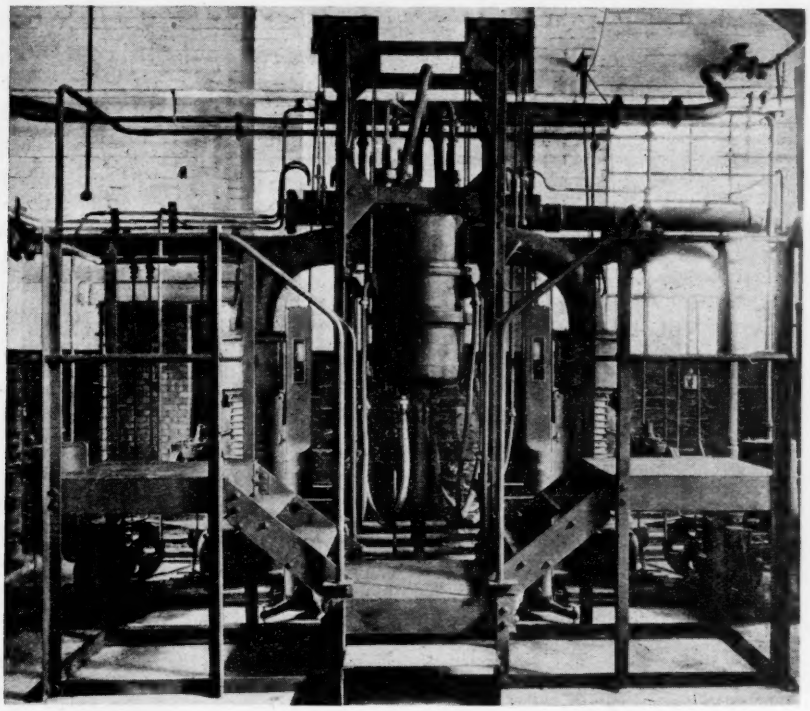

Fig. 6. Furnace for sintering tantalum.

It is interesting to note the time Siemens & Halske required to sinter. The three sintering schedules were (1) evacuate furnace to 0.001—0.002 mm. Hg and raise temperature to 2,300°C. in about 20 minutes, and maintain for 15 minutes, (2) evacuate furnace and raise temperature to 2,400°C. in 2 hours and maintain for 16 hours ; the pressure at the end of this period is 0.01—0.02 mm. Hg, (3) evacuate furnace to 0.001—0.002 mm. Hg and raise temperature to 2,300°C. as rapidly as possible, maintain at 2,300°C.

for 2 hours and raise to 2,500 °C. and maintain for 12 hours ; the pressure at end of this period is 0.02 mm. Hg. It is very probable that the excessive sintering periods were due to the lack of pumping capacity. The process as operated at Murex requires sintering periods which are a fraction of those employed by Siemens, although the weight of the pressed bars being sintered is probably more than that used by Siemens & Halske. During the sintering operation

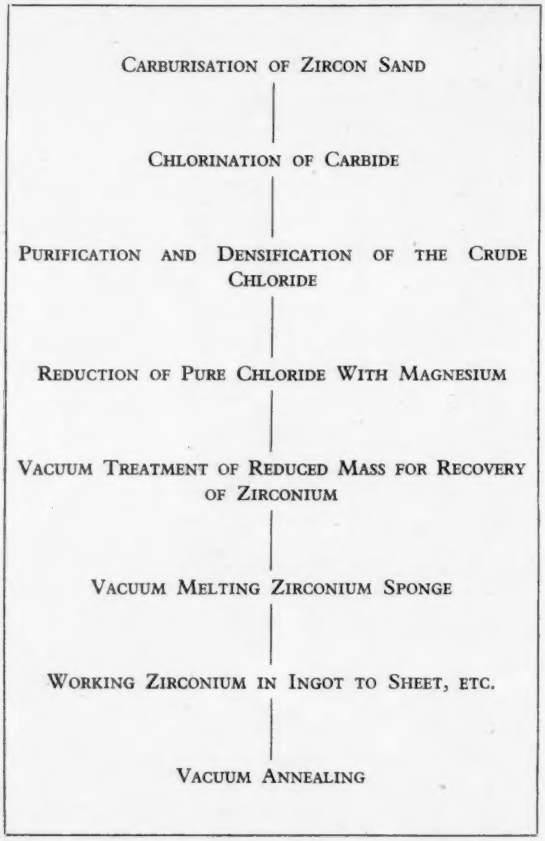
Carburisation of Zircon Sand
Chlorination of Carbide
Purification and Densification of the Crude Chloride
Reduction of Pure Chloride With Magnesium
Vacuum Treatment of Reduced Mass for Recovery of Zirconium
Vacuum Melting Zirconium Sponge
Working Zirconium in Ingot to Sheet, etc.
Vacuum Annealing

Fig. 7. Flow Sheet of the zirconium production process.

there are three stages of gas evolution, the first which occurs about 450-650 °C. is due to the evolution of absorbed hydrogen, the second, which occurs about 1,500 °C. is probably due to the reduction of some oxide by the small amount of carbon present in the metal powder, the final gas evolution stage occurs at 2,000-2,300 °C. and is due to the evolution of a lower oxide of tantalum. All these gassing stages take time and it is desirable to provide pumping equipment capable not only of producing a high ultimate vacuum but, in addition, possessing a high pumping capacity. If the pumping capacity is small, then pumping time must be excessive and the process becomes uneconomical. Realising the importance of pumping capacity the plant at Murex was designed to give the maximum. An eight-inch oil diffusion pump with a pumping capacity of 500 litres per second at a pressure of 10^{-4} to 10^{-5} mm. Hg was connected to the furnace and the backing was provided by a rotary mechanical pump, similar to that used on the Murex magnesium process, with a capacity of 110 cubic feet per minute. The ultimate vacuum obtained before attaining top temperature was 0.001 mm. Hg as measured by a Pirani thermocouple gauge and 0.003 to 0.0005 mm. Hg measured on a McLeod gauge.

After sintering, the bar of tantalum is fabricated to the usual forms, but if hardening occurs due to working, then it is necessary to anneal by heating to about 1,500 °C. in a high vacuum.

The commercial production of zirconium has created considerable interest in the literature and it has been fully appreciated that the development of the process has resulted largely from improvements in the construction of large vacuum vessels and pumping equipment.

Zirconium is extremely reactive towards most gases and it is essential, if ductile metal is to be obtained, to avoid the presence of all but the truly inert gases such as argon and helium, when the metal is at temperature above 300 or 400 °C. If contamination due to the presence of gases such as oxygen and nitrogen occurs, the metal is embrittled and cannot be fabricated to useful forms.

Two processes, both employing vacuum techniques are now in use for the production of ductile zirconium on a commercial scale. One of the processes is based on the thermal decomposition of zirconium tetraiodide ; it is known as the Iodide or Van Arkel Process.

Crude zirconium is heated in a vacuum vessel in

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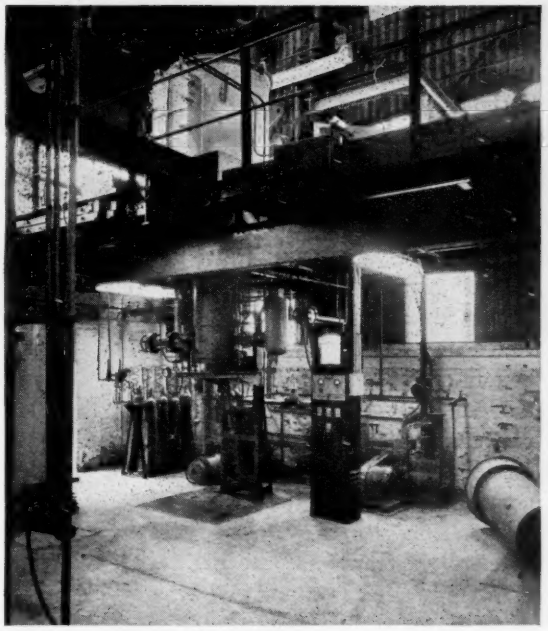
Fig. 8. Vacuum furnace for eliminating magnesium chloride from reduced zirconium.



the presence of iodine vapour. A reaction occurs with the formation of gaseous zirconium tetraiodide which decomposes on contacting a hot filament in another part of the vessel. The zirconium metal formed by the decomposition is deposited on the filament, while the iodine vapour reacts with more crude zirconium. The cycle is repeated continuously until a finger-thick rod of pure zirconium metal is built up. Published accounts of the process contain little detail of the vacuum system.

The second, or Kroll, process used for the production of zirconium is being operated in the United States and England. This process, unlike the first, has been described in fair detail in several publications. The basic principle of the Kroll process is the reduction of zirconium tetrachloride vapour with magnesium, but this is only the first step in the process and it is necessary to recover the reduced metal free from the salts produced during the reduction.

The reduction is carried out in a heat-resisting vessel in an atmosphere of argon. The magnesium is melted in a steel crucible and the zirconium tetrachloride heated until it sublimes. The tetrachloride vapour is reduced by the molten magnesium and at the end of the reaction the crucible contains a mixture of zirconium metal, magnesium chloride, and a little magnesium which was added in excess to ensure complete reduction of the chloride. After cooling, the reaction crucible and its contents are removed from the vessel.

In the case of titanium, which is produced by a very similar process, the reduced mass is machined out of the crucible and the mixture of titanium and magnesium chloride in the form of coarse turnings are leached with dilute hydrochloric acid to remove the salt and unreacted magnesium. It is essential during this operation to cool the liquor to avoid undue oxidation of the titanium powder. After leaching and washing the titanium powder is dried at a low

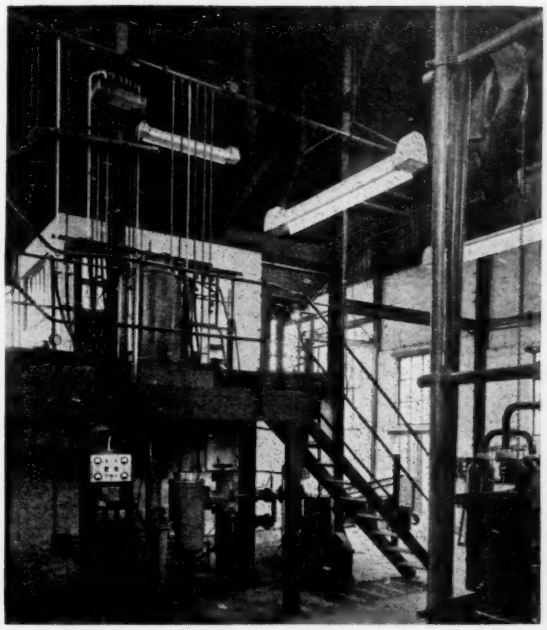


Fig. 9. Vacuum furnace for melting zirconium sponge.

temperature. Titanium produced by this technique still contains appreciable quantities of magnesium. In addition, hydrogen which is produced during the leaching operation, is absorbed by the metal and leads to difficulties in the later stages. As a result of the difficulties encountered during the leaching of the reduced titanium, it was decided, in the case of zirconium, to use a vacuum technique. The crucible containing the zirconium mixed with magnesium chloride and magnesium is inverted, placed on a long steel tube and raised into the upper part of an inverted steel retort. The cover which seals the open bottom-end of the retort, supports the tube carrying the crucible. The retort is evacuated to a low pressure and the upper section containing the crucible is heated by a surrounding furnace. The temperature is raised to about 950°C. while the vacuum is maintained.

In order to reduce the danger of the hot steel retort collapsing a partial vacuum of 1-2 mm. Hg is maintained in the heating furnace.

Under the reduced pressure the magnesium distills into the bottom end of the retort, where it collects on thin steel condensers fitted closely to the water-jacketted walls of the retort. The magnesium chloride is removed partially by melting and draining away from the charge and partially by vaporising from the mass.

The pressure obtained after degassing the mass is about 0.1 micron Hg as measured by an ionisation gauge.

The vacuum system consists of an oil diffusion pump backed by a mechanical pump. High pumping capacity is essential to deal with gases, including water vapour, which are evolved during heating. The system must be evacuated rapidly and maintained at a very low pressure to ensure that the reactive zirconium is not contaminated with impurities such as oxide which would render the metal brittle and useless. Exact and cautious measurement of temperature and pressure is required to ensure a satisfactory product. Thermocouple gauges connected to recorders have been found very satisfactory for the main operation but in the final stages an ionisation gauge is necessary to measure the low pressure.

To maintain the high vacuum it is necessary to use a cold trap which prevents contamination of the pump oil with water vapour.

The time required for the treatment in vacuum is determined experimentally and on completion the heaters are switched off and the retort and its contents allowed to cool to room temperature. After breaking the vacuum the retort is opened and the crucible removed. The crucible now contains a greyish mass of sintered metal which is removed and cut into small pieces preparatory to the next operation.

The sintered metal, or sponge, still contains a little magnesium and magnesium chloride which could greatly impair its properties, but in any case, the zirconium in this condition cannot be worked and it is necessary to convert it to sound metal by melting and casting. During the melting and casting operations it is essential to avoid combination with the common gases and this is best achieved by melting in a vacuum vessel. The low pressure system also ensures the removal of the last traces of magnesium and magnesium chloride from the sponge.

Carbon is used as the melting crucible material because zirconium is so reactive at high temperatures that it reduces all the known refractories and while a little carbon is absorbed during melting it is not sufficient to affect greatly the final properties.

Zirconium has been melted satisfactorily using split-tube graphite resistor furnaces. This type of furnace attains the comparatively high melting temperature rapidly and easily. The split-tube furnace is contained within a steel vessel which, when closed and sealed by rubber gaskets, can be evacuated to a low pressure. The vacuum system used on the melting furnace is the same as that described for the vessel used for the removal of the magnesium and magnesium chloride from the reduced zirconium.

An oil diffusion pump backed by a mechanical pump is connected to the furnace with a cold trap in the line between the vacuum vessel and the diffusion pump. High pumping capacity is combined with the ability to pump to a low ultimate pressure. The high pumping capacity is required as the temperature rises very rapidly and the evolved gases must be removed as quickly as they are produced to maintain

the low pressure required for the production of the highest grade metal. During the melting the magnesium and magnesium chloride present as impurities are vaporised and collected on a special condenser. The use of the condenser prevents the walls and metal baffles of the furnace being contaminated with hygroscopic magnesium chloride. The hygroscopic salt absorbs large quantities of water vapour when exposed to the atmosphere and if the salt were permitted to contaminate the vacuum vessel it would be almost impossible to obtain satisfactory evacuation. For the same reason it is necessary to clean the retort after the treatment for the removal of the salt.

The pressure as measured by an ionisation gauge during the melting of the zirconium is 0.3 to 0.5 micron Hg.

The final processing of the zirconium from the cast ingots to sheet is accomplished by hot working. Protection from oxidation is achieved by the use of gas-tight steel sheaths which are forged and rolled with the enclosed ingot.

Some cold working is necessary to produce a satisfactory finish on the metal. The cold working causes work-hardening of the zirconium and it is sometimes necessary to anneal before processing further. While some degree of annealing may be obtained by heating for a short period at 650°C. in air, it is necessary to heat at a higher temperature for a longer period out of contact with the common gases to produce fully annealed metal. Annealing may be performed in argon or *in vacuo*. If argon is used it is essential to remove the residual nitrogen present in the gas. Purification of argon on a commercial scale is difficult, and generally it is considered better to anneal zirconium in a vacuum furnace. The annealing temperature is about 750°C. and a period of 30 minutes at a pressure not exceeding 2 microns Hg is recommended.

RESUME

Magnesium, calcium, tantalum, and zirconium are all reactive metals, and at comparatively low temperatures they combine with many of the common gases such as oxygen, nitrogen and hydrogen. Contamination of the metals by reaction with such gases results in deterioration of the properties of the metals. Such contamination is avoided by the use of vacuum techniques.

In addition to the protection provided by the use of vacuum equipment other advantages are obtained. In the case of magnesium and calcium the reduction reaction takes place at a temperature above the boiling point of the metal at the operating pressure, thus greatly facilitating the removal of the metal from the products of reduction.

Tantalum provides an interesting example of the use of vacuum in metallurgy. The tantalum powder which is used in the production of sheet and other forms of the metal contains several impurities ; hydrogen, carbon, and oxygen all being present. The removal of all these impurities is greatly facilitated by the use of low pressures during the sintering operations.

There can be little doubt that the successful production of ductile zirconium depends on the efficiency of the vacuum system. Small quantities of oxides and similar impurities render the metal brittle, and it is essential to perform all operations on hot zirconium out of contact with the common gases.

The use of a vacuum retort for the removal of magnesium chloride and magnesium from the reduced zirconium is to be preferred to the leaching operation used in the earlier titanium work. The metal is received as a sintered mass containing a little residual magnesium and magnesium chloride which are removed during the melting operation under vacuum.

The above examples illustrate the successful application of vacuum techniques to metallurgy. It has been demonstrated that not only does the use of vacuum provide protection during the processing of reactive metals but it also provides a means of removing volatile impurities or even the recovery of a volatile metal from non-volatile impurities.

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An assessment of some WORKING FLUIDS FOR DIFFUSION PUMPS

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Summary

SINCE OILS were first suggested as alternatives to mercury as pumping fluids for diffusion pumps, a very large number of organic and semi-organic materials have been applied to this use. All these have differing characteristics which may affect the choice of fluid for a particular application, while the use of mercury itself is still essential in some cases and desirable or at least defensible in others.

The authors discuss how some of the characteristics of a selection of pumping fluids would influence a user in his choice, and illustrate the discussion with some of their own experiences and experiments.

Sommaire

DEPUIS QUE DES HUILES furent pour la première fois suggérées comme alternative au mercure, comme fluide de pompage pour pompes à diffusion, un très grand nombre de matières organiques et semi-organiques ont été appliquées à cet usage. Elles ont toutes des caractéristiques différentes ce qui peut influencer le choix du fluide à utiliser en vue d'une application particulière, tendis que le mercure luimême est toujours indispensable dans certains cas ou du moins désirable ou simplement admissible dans d'autres.

Les auteurs discutent, comment certaines de ces caractéristiques d'un choix de fluides de pompage influenceraient l'utilisateur dans son choix et citent à l'appui de cette discussion, quel-ques-uns de leurs propres essais et expériences.

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INTRODUCTION

UNTIL 1928 the only operating fluid in general use in diffusion pumps was mercury. It was then that C. R. Burch[1] succeeded in distilling certain low-vapour pressure fractions of naturally occurring hydrocarbon oils and in applying them as diffusion pump fluids which, for certain purposes, exhibited some striking advantages over mercury. Burch's early work was quickly followed up by K. C. D. Hickman, [2, 3] who applied certain esters of phthalic and sebacic acids for the same purpose, and synthesised and purified higher and more phlegmatic esters especially for use in diffusion pumps.

Since then, a large number of organic substances which may loosely be termed oils have been tested with varying success as diffusion pump fluids, but only two groups, in addition to refined hydrocarbon oils and the esters, have been at all widely used. These are the Aroclors (chlorinated biphenyls) and, most recently of all, the semi-inorganic silicone fluids.

Although oil diffusion pumps have been known for over 20 years, it is only in the last decade that they have been really widely applied in research and industry. Their application has been very largely successful, but there have been certain cases where disappointing results (often traceable to ignorance of their characteristics) have produced a certain reaction in favour of mercury and in other fields mercury has remained unchallenged.

In use, of course, the oils have some characteristics totally different from those of mercury and they also differ significantly from one another. It is the intention of this paper to make an interim assessment of some characteristics of a number of well known pumping fluids and to discuss factors influencing the choice of fluid for various applications. The authors

*M.S. received July, 1952.

have obtained their information from their experience and experiments, from the literature and from personal contacts with other users of vacuum equipment. The personal bias of the individual worker is often a powerful factor influencing selection—but the authors have tried to be as objective as possible.

It should be remembered throughout the discussion that a particular fluid may behave very differently in pumps of differing design. The oils are particularly sensitive to variations in pump design, and a disappointing performance may often be attributable to an unsuitable pump rather than to an unsuitable fluid. The authors have discussed some of the influences of pump design in an earlier paper.[4]

THE RELEVANT CHARACTERISTICS OF MERCURY

The only major disadvantage of mercury is its comparatively high vapour pressure—about a micron at ordinary temperatures. Of secondary importance are its tendency to amalgamate with certain materials which might otherwise be used for pump construction, and the peculiar sensitivity of mercury pumps to traces of oil or grease contamination*.

On the credit side, mercury is an element which cannot decompose, however hot the pump boiler may run and is unlikely to react with most gases or vapours which may be pumped. The vapour arising from mercury is a known vapour easily recognisable in the system being pumped, incapable of decomposition on filaments and without any content which cannot readily be trapped out with liquid air. Mercury readily releases any gases and light vapours which may be initially dissolved in it, and it is easily purified by distillation. A further merit of the liquid is its high density which facilitates its return to a boiler running at high pressure. For example, a pump capable of operating at 40 mm. Hg backing pressure may require a boiler pressure of 120 mm. Hg. A fall tube of 15 cm. length would suffice to return fluid to the boiler in the case of a mercury pump, but for an oil pump of similar performance a fall tube over 2 metres long would be required.

A mercury pump must normally be made of glass or steel and both pump and fluid must be thoroughly degreased before use; a refrigerated trap is essential if really low pressures are desired. Unless a severe loss of pumping speed can be tolerated, this trap must be virtually as big as the pump and the cost of its operation must be carefully considered when designing a system. But a mercury pump may be made to operate with a backing pressure of 40 mm. Hg or more, and decomposition products of the fluid will be entirely absent from both fine and backing sides. A carefully cleaned pump will ' condition ' rapidly to give a low pressure and if an efficient liquid air trap is used it is likely that the contribution from the pump to the total pressure above the trap will be relatively small.

THE ORGANIC FLUIDS AS A GROUP

Organic fluids for the operation of pumps are available with vapour pressures at ordinary temperatures varying from about 10^{-4} to the order of 5×10^{-8} mm. Hg. These fluids are sufficiently inert with respect to most metals to permit a wide selection of materials to be used for pump construction, and pumps working with these fluids are insensitive to contamination in the sense that they will operate correctly even though they have been very indifferently cleaned, (though the ultimate may of course be affected). Moreover, although the purification of organic fluids in bulk is much less easy and more expensive than in the case of mercury, it is possible to design the pump in such a way that, when charged with a suitable crude fluid, it will itself perform much, if not all of the necessary purification. The major disadvantage of the fluids is that they are all complicated chemical structures and are all subject to some chemical decomposition under any one of a number of conditions normally encountered during use.

*Unless the most scrupulous care is exercised in cleaning, the speed of a mercury pump may be reduced by such contamination to a small fraction of its normal value—probably because of the inefficient evaporation and condensation of mercury contaminated by grease films[5]. Because mercury boils at a lower temperature than most oils or greases, mercury pumps cannot be made self-purifying in the sense that oil pumps can.

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Continuous gradual decomposition always occurs in the pump boiler (it may be accelerated by the catalytic action of some constructional materials) and though this is normally insignificant from the point of view of fluid wastage, it provides a supply of gaseous and vaporous decomposition products which emerge continuously from both the high vacuum and backing ports of the pump.

Decomposition of pumping fluid vapour will also occur on hot filaments or in an electric discharge in the system above the pump, and this may produce solid deposits as well as vapours and gases.

Most of the fluids decompose so severely if exposed to air at atmospheric pressure whilst at working temperature, that the whole fluid charge may become unfit for further use after a few such exposures.

Oil pumps can produce pressures certainly of the order of 10^{-7} mm. Hg without the aid of any refrigerated trap—but the contribution from the pump to the pressure in the system will consist of a mixture of largely unknown vapours and gases.

Comparatively mild refrigeration can be made to produce a very considerable reduction even in this low pressure, but there will still be some permanent gas contribution from the pump which no cold trap can stop.

Because the fluid decomposition rate increases with boiler temperature and pressure, it is unusual for oil diffusion pumps to be made to operate with limiting backing pressures much in excess of $\frac{1}{2}$ mm. Hg, though it is perfectly possible to design an oil pump with a backing pressure of several mm. Hg if the extra decomposition is not considered objectionable and very low ultimate pressures are not required.

The ultimate pressure obtained with a particular organic fluid is as dependent on the efficiency of any fractionating or purifying arrangements built into the pump as it is on the properties of the fluid itself, and some of the qualities of a fluid can only be assessed in relation to those of the pump, in which it is used.

SOME COMPARISONS OF A NUMBER OF ORGANIC FLUIDS

The following comparisons are based almost entirely on the authors' own experience. Their information is much less complete than could be desired, but it has seemed worth while to present it at this stage. Some well known fluids are omitted because the authors are not sufficiently familiar with them, but the selection discussed is broadly representative. The properties which most concern us

Table I. **Relevant Properties of the Fluids Considered.**

Fluid	Chemical Nature	Formula	Molecular Weight	Vapour Pressure mm. Hg	Temp. °C
Apiezon B	Hydrocarbons	..	*	10^{-7}	R.T.
„ C	„	..	*	10^{-8}	R.T.
„ G	„	..	..	10^{-6}	R.T.
„ BW	„	..	*	10^{-7}	R.T.
G.A.B. Diffusion Pump Oil 6	„	..	..	10^{-6}	R.T.
D.C. 702	Methyl Polysiloxanes	..	530	..	..
„ 703	„ „	..	570	..	..
Octoil S	Di-2-Ethyl Hexyl Sebacate	$C_8H_{16}(COOC_8H_{17})_2$	426	5×10^{-8}	25
Narcoil 20				3×10^{-8}	25
Narcoil 10	Chlorinated Diphenyls	..	326	3×10^{-4}	25
Commercial Plasticiser	Tri-m-Cresyl Phosphate	$Ch_3C_6H_4)_3PO_4$	368	3×10^{-8} † / 9×10^{-8} ††	25
„ „	Tri-Xylenyl Phosphate	$((CH_3)_2C_6H_1)_3PO_4$	414	..	..
„ „	Glycerol	$(CH_2OH)_2CH(OH)$	92	5.6×10^{-5} §	15

† See Ref. 8. †† See Ref. 9. § See Ref. 15

* See article by G. Burrows, in this issue, page 50

Manufacturers claims of vapour pressure are normally obtained by extrapolation, *e.g.* Ref. 10.

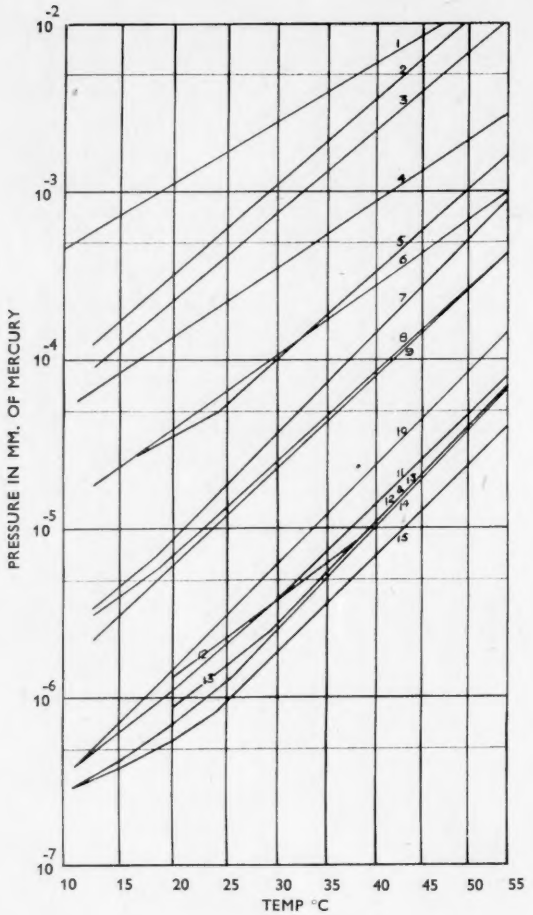

Fig. 1. Temperature-pressure curves for various fluids used in F203.

Key

1. Mercury
2. Arochlor 1254
3. Narcoil 10
4. Edwards 8A Rotary Pump Oil
5. G.A.B. Diffusion Oil 6
6. Apiezon G
7. Silicone 702
8. Apiezon B
9. Apiezon BW
10. Silicone 703
11. Tri-Cresyl Phosphate
12. Di-2-Ethyl Hexyl Sebacate
13. Octoil S
14. Tri-Xylenyl Phosphate
15. Apiezon C

are the ultimate pressures obtainable and the chemical stability.

(1) Vapour Pressure and Attainable Ultimate Vacuum

The absolute vapour pressures at room temperature of the organic fluids cannot be measured easily. They are usually estimated by extrapolation of measurements at higher temperatures and manufacturers' claims are usually based on such estimations. The ultimate vacua obtainable are usually measured with an ionisation gauge calibrated for air. Such gauges are probably about ten times more sensitive to oil vapours than to air, though the calibration constants are not known with any accuracy. If, then, a high speed gauge is used so that tubulation errors are avoided,[6] the pressure recorded using the air calibration may be several times higher than the true pressure. It has become conventional, however, to accept the readings of the air calibrated gauge for comparison purposes.

Fig. 1 presents temperature-pressure curves for a chamber pumped by a three-stage metal fractionating pump (Speedivac F203) using various organic fluids, pressures being measured with a high-speed air-calibrated ionisation gauge (for a complete description of the method and pump see Ref. 4). If a non-fractionating pump had been used, the results would have been very different. If a multi-boiler glass fractionating pump had been used, since the temperature in the boiler supplying the high vacuum stage could have been reduced, catalytic action associated with constructional metals eliminated and greater cleanliness achieved, lower pressures might have been reached[7]. However, with the reservations implied above these curves are fair representations of what can be expected from the use of the fluids in a good practical fractionating pump.

Table 1 presents manufacturers' claims for the vapour pressures of the proprietary fluids at ordinary temperatures, and estimates of the vapour pressure of tri-cresyl phosphate.[8,9]

The plasticisers, tri-cresyl and tri-xylenyl phosphate and di-ethyl hexyl sebacate and the fluid Aroclor are of commercial quality and not specially purified for high vacuum use. Octoil S and Narcoil 10 are specially purified chemical equivalents of di-ethyl hexyl sebacate and Aroclor 1254 respectively.

(2) Decomposition in Normal Operation at High Vacuum

All the organic fluids are subject to gradual decomposition when used under normal conditions in a pump producing a high vacuum. This decomposition may be so gradual as to be negligible from the point of view of fluid wastage—but the products of decomposition may greatly influence the ultimate vacuum, especially with non-fractionating pumps, and any gaseous products must limit the extent by which refrigeration can reduce the ultimate pressure obtained. The extent to which hydrogen is produced may affect the possible sensitivity of leak testing systems employing a hydrogen probe.

The rate of decomposition must depend on the boiler temperature and on the extent to which constructional materials behave as catalysts, while the degree to which undesirable products reach the fine side must depend on the pump design. Any order of merit, then, assigned to the fluids could relate only to exactly specified conditions of use.

No such assessment has in fact been made. Hickman and Sanford[2] have measured the pressure rise at various temperatures in sealed glass vessels partly filled with some fluids. Blears[11] has shown how the mass spectrometer can be used to analyse the atmosphere in a vessel being pumped and to measure the partial pressures of the various gases and vapours present, and he has compared the atmospheres in systems pumped by oil pumps using Apiezon C and Apiezon BW and by mercury pumps—but his published work is intended primarily to demonstrate some uses of the mass spectrometer and is not sufficiently extensive to provide the basis for a full comparison. Another approach might be to measure the pressure rise in a backing capacity, into which a diffusion pump would compress nearly all its volatile decomposition products. Some analysis of the products collected could also be made.

The authors have frequently trapped out by refrigeration the vapour components in headers containing high speed ionisation gauges. A big reduction in indicated pressure has been taken as evidence that the gas pressure from all sources—including leakage and decomposition—was relatively small. Such a test is open to too many objections to allow the results to be advanced in this connection, but they do indicate clearly that gaseous decomposition products issuing from the top jet can in certain cases impose a very definite limitation on the extent to which the pressure above an oil pump can be reduced by refrigeration.[4]

(3) Decomposition on Exposure to the Atmosphere of Fluids at Working Temperature

Resistance to decomposition on exposure to the atmosphere whilst hot is a measure of the general ruggedness of the fluids in ordinary use. The organic fluids are usually guarded from such exposure, but it frequently occurs due to accident and is responsible for a great deal of fluid wastage. Fluids differ greatly in the extent to which they will survive repeated exposures of this sort as useful pumping agents, and any considerable decomposition is accompanied by the fouling of the pump interior with carbonaceous and tarry deposits which are difficult to remove.

Again, no precise order of merit can be assigned to the fluids without most carefully controlling and specifying the experimental conditions ; but the authors have made some tests which, although open to many objections, do give a useful idea of what may be expected in practice.

A chamber of a few litres capacity was evacuated by a standard $2\frac{1}{4}$ inch diffusion pump (Speedivac 203) containing the fluid to be tested. After 15 minutes pumping, the pump heaters were switched off, a valve in the backing line was closed and a second valve admitted air to the pump and the chamber. After 5 minutes of such exposure the valves were returned to their original positions, the heaters were again switched on and pumping was resumed for a further 15 minutes, the chamber being roughed down through the hot pump. This cycle of alternating exposure and pumping continued until a cold cathode ionisation gauge mounted on the chamber indicated that the pump had stopped pumping and that breakdown of the fluid was substantially complete. The apparatus is illustrated in Fig. 2.

Table II. **Fluids Arranged in Ascending Order of 'Ruggedness' as Determined by the 'Breakdown' Tests.**

Fluid	Number of Cycles		Remarks
	1st Run	2nd Run	
Apiezon C	160	205	
Apiezon BW	279-307		
Octoil S	230	376-395	
Di-2-Ethyl Hexyl Sebacate	323-359	302	
Tri-Xylenyl Phosphate	368-430	566-583	
G.A.B. Diffusion Pump Oil 6	530		Pumps failed due to the decomposition of the residual oil
Tri-m-Cresyl Phosphate	574-582	516-583	
Apiezon B	491-504	670-714	
Narcoil 10	964-980		Pumps failed due to the total loss of oil to the backing pump
D.C. 703	1,100		
D.C. 702	500	1,516	Tests discontinued before failure

* The runs with D.C. 702 were never continued to the failing point. In both cases the pumps were run until only 50% of the original charge was left, the second run being carried out with a special trap in the backing line to limit the carry-over of fluid to the rotary pump. An amber colouration was the only change in the appearance of this fluid, this colour being light in the case of the 500 cycle and deep in the case of the 1,516 cycle run.

An important objection to the test method is that a small amount of fluid is carried over from the diffusion to the backing pump each time the chamber is roughed down—so that final failure to pump comes when the sum of two losses, that by decomposition and that through the backing line to the backing pump have reduced the fluid charge below the working minimum. The apparatus was set up precisely because of this feature—to investigate the total loss of fluid during the valveless pumping of cathode ray tubes (see below) and was only subsequently used as a rough and ready means of assessing the ruggedness of a number of fluids.

The results are presented in Table 2 and a photograph of a number of pump jet assemblies after being used to test various fluids is presented in Fig. 3.

The silicone fluids and Narcoil 10 stood up to the treatment so well that the pump interiors remained substantially clean and pumping would only cease when too little fluid remained in the pump to operate it. All the other fluids exhibited very heavy decomposition, and gross fouling of the pump interiors occurred. Where tests were repeated, results were usually consistent within the very rough limits of the experiment. In Table 2 the oils are arranged in a rough order of ascending ruggedness as revealed by the tests. It should be pointed out that boiler temperature varies from fluid to fluid so that a fluid like Apiezon C experiences a considerably higher temperature in the boiler than does, say, Narcoil 10. Low vapour pressure is a handicap from the point of view of the test.

An interesting feature was that in every case the system continued to be pumped to 10^{-4}mm. Hg, or lower, each brief pumping cycle right up to a few cycles before final breakdown. In one or two cases cycling was preceded by a pump-down test and was later interrupted for further pump-down tests with a high-speed hot-cathode gauge. The results are presented in Table 3. The pump used seems able to rid itself substantially of volatile decomposition products even in the presence of very heavy tarry and solid deposits.

Table III. **Ultimate Pressures Measured at Intermediate Stages During the 'Breakdown' Tests.**

Fluid	Number of Cycles	Ultimate Pressures In mm. Hg (Air Equivalent)	Temperature °C
Octoil S	0	5.8×10^{-6}	21.5
	135	9.2×10^{-6}	21.5
	230	Complete Breakdown	
Apiezon BW	0	1.25×10^{-5}	17.8
	120	$3. \times 10^{-5}$	16.5
	240	3.7×10^{-5}	17.5
	279-307	Complete Breakdown	
D.C.702*	0	1.3×10^{-5}	22
	545	1.7×10^{-5}	22
	1,104	2.2×10^{-5}	22
	1,516	2.04×10^{-5}	21.5

* D.C. 702 never broke down and in this case alone a trap was used to reduce the loss of fluid to the rotary pump. After 1,516 cycles 50% of the original charge had been lost.

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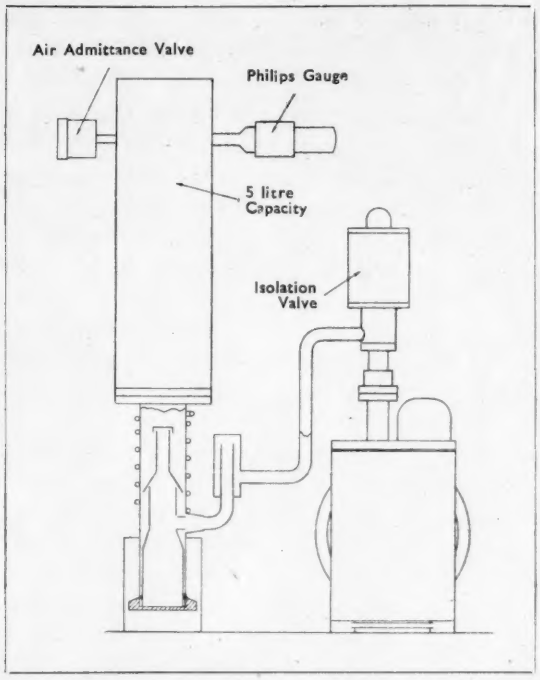
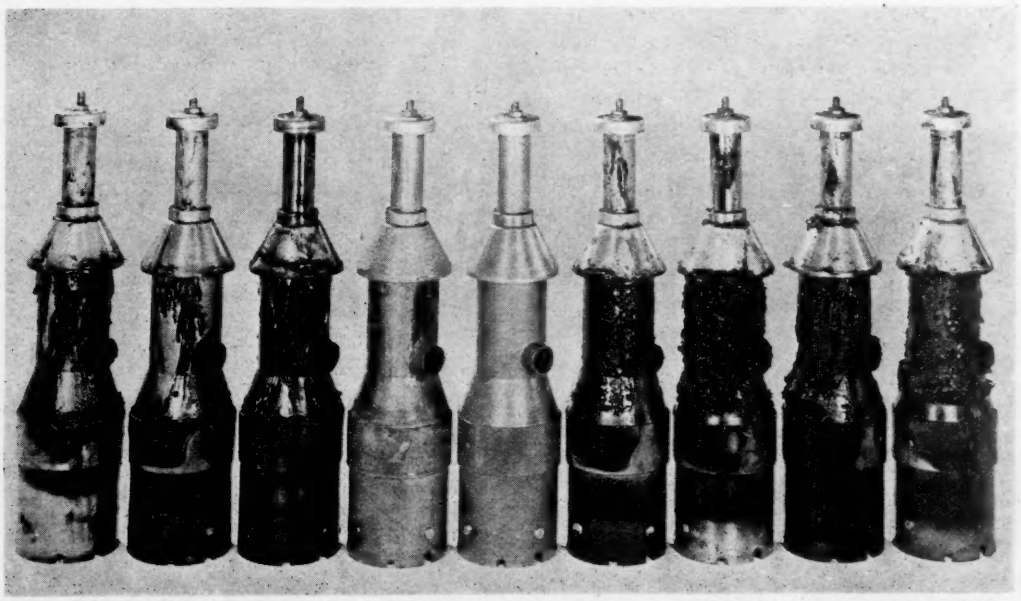


Fig. 2. Apparatus used to compare the resistance to breakdown of fluids during quick cycle valveless pumping.

Fig. 3. The photograph (below) shows the jet assemblies of the diffusion pump on the 'breakdown set' after use with different fluids. The number of cycles completed before the jet assemblies were removed is indicated below each fluid.



(1) Tri-Xylenyl Phosphate 583 cycles | (2) Tri-Cresyl Phosphate 570 cycles | (3) Octoil S 395 cycles | (4) Narcoil 10 980 cycles | (5) Silicone 703 1,100 cycles | (6) Apiezon C 205 cycles | (7) Apiezon BW 307 cycles | (8) Apiezon B 714 cycles | (9) G.A.B. Diffusion Oil 6 530 cycles

Key to Fig. 3

(4) The Effects of the Oil Vapours in the System Being Pumped

The advisability of using oil pumps to evacuate continuously-pumped apparatus containing emitting filaments or in which electric discharges occur, or to evacuate apparatus containing photo-sensitive or secondary - emission surfaces has been widely questioned. Organic vapours must decompose on a hot filament, or under bombardment by electrons. They are likely to poison coated or thoriated filaments and sensitised or secondary-emission surfaces, particularly when these are subjected to electron bombardment. A. Lempiski and A. B. McFarlane[12] report adversely on the effects of the decomposition of D.C. 703 vapour on bombarded secondary emission surfaces, but offer no comparison with the vapours of other fluids. G. Herrmann and O. Krieg[13] have investigated the effects of some gases and some of the simpler hydrocarbon vapours, such as might be produced by hydrocarbon oil decomposition, on oxide coated cathodes. In some cases these effects may prohibit the use of oil pumps, in others they may be insignificantly slight. The use of untrapped oil pumps as opposed to mercury in these cases will be discussed below, and the authors must admit that they can make no adequate comparison at all of the qualities of the individual organic fluids in this respect, but a few remarks may be offered.

Any effect a vapour may have in a system is likely to vary with its concentration in the system. If the use of an oil pump is to be attempted in a doubtful case, a fluid with the lowest possible vapour pressure should, therefore, be selected and should be used in a good, well baffled fractionating pump. This may reduce the vapour concentration several hundred times. The authors have found that high-speed ionisation gauges using plain tungsten filaments suspended directly above the baffle in the pump mouth have a satisfactorily long life when a very low vapour pressure oil is used in a fractionating pump—and maintain their calibration. The same gauges have a limited life with less suitable fluids and pumps and may suffer calibration changes during their lifetime.[4]

When an organic vapour is severely decomposed in a discharge or on a surface bombarded by electrons some solid deposit may occur. With most organic vapours this deposit takes the form of a carbonaceous film, which may be conducting or insulating, according to the manner of its formation, but with the silicone fluids the deposited film is likely to be of insulating silica. Suitable choice of fluid will avoid the least welcome risk. The authors have incidentally found no evidence that hot cathode ionisation gauges are specially prone to change their calibration in silicone vapour due to the formation of insulating films, and have been informed that early reports of this effect were almost certainly occasioned by the behaviour of an impurity present in very early batches of silicone fluids and since eliminated.*

(5) Pumping Speed and Limiting Backing Pressure

The speed curves presented in Fig. 4 were taken with a standard 2¼ inch bore 3-stage pump (Speedivac 203) with the normal input of 250 watts and using an ionisation gauge. The ' intrinsic' speed† is indicated by the approximately level part of each curve to the left of the ordinate where the curve takes a downward plunge as the point is reached where the top stage ' breaks down '. The speed curve for a mercury pump (Speedivac 2M2) of the same bore and admittance area as the oil pump has been added to Fig. 4 to correct a wide spread impression that

*Private Communication from Dr. S. L. Bass, Dow Corning Corp.

†At low pressures the measured speeds have been corrected by the use of the formula

Intrinsic Speed × (Measured Pressure—Ultimate Pressure obtained before testing)
= Measured Speed × Measured Pressure[14]

the pressure difference on the left hand side of the formula being taken as the abscissa when plotting. This was done because it would have taken too much time to achieve the lowest pressure, of which each fluid was capable before each speed test and uncorrected comparisons might have been unjust.

The correction is usually small over the pressure range covered by the curves and becomes negligible at the higher pressures.

Where the intrinsic speed and the ultimate pressure are known, the above formula can be used to produce a ' practical ' speed curve right down to the ultimate pressure in close agreement with that which would be obtained by measurement.

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mercury pumps necessarily have lower intrinsic speeds than oil pumps.

The maximum throughput of air obtainable at the intrinsic speed is given in litre microns/sec. by the product of this speed and the pressure in microns where the downward plunge begins. The throughput is substantially constant throughout the downward plunge, which thus represents a region of pressure instability.

It would be quite inadmissible to use the curves as evidence that a particular fluid is superior to any other with regard either to speed or to maximum throughput. Both the heater input and the design of the pump selected for the test must favour some fluids more than others and it is the authors' repeated experience that any order of merit established during one series of measurements may be completely contradicted by a second series for which these two conditions have been varied.

With regard to speed, there may be inherent differences in the fluids which should give one an absolute advantage over another if both could be used ideally, but any such differences are at present completely masked under practical test conditions. With regard to throughput, the more volatile fluids are probably superior if the fluids are compared in a single-stage pump backed by a fore pump of consistent performance—but in a multi-stage pump this is no longer certain, since the performance of every stage may vary with the nature of the fluid and the top stage is no longer 'backed' consistently during a series of tests with different fluids.

The real value of the curves is that they demonstrate the enormous variety of fluids which an oil pump can employ whilst continuing to give substantially similar speed curves. From glycerol* and

*With certain pumps it may be necessary to reduce the heater input when employing comparatively volatile fluids like glycerol, to prevent the boiler pressure becoming excessive. The use of glycerol is not advised, however. Its vapour pressure is high, and this and its low molecular weight make it difficult to baffle. Pumps left standing containing the fluid become quickly contaminated with water due to its hygroscopic nature. If of steel they may rust quickly. A case for the use of glycerol has been made by P. Alexander and the fluid has been successfully used in glass pumps fitted with liquid air traps as for mercury.[16]

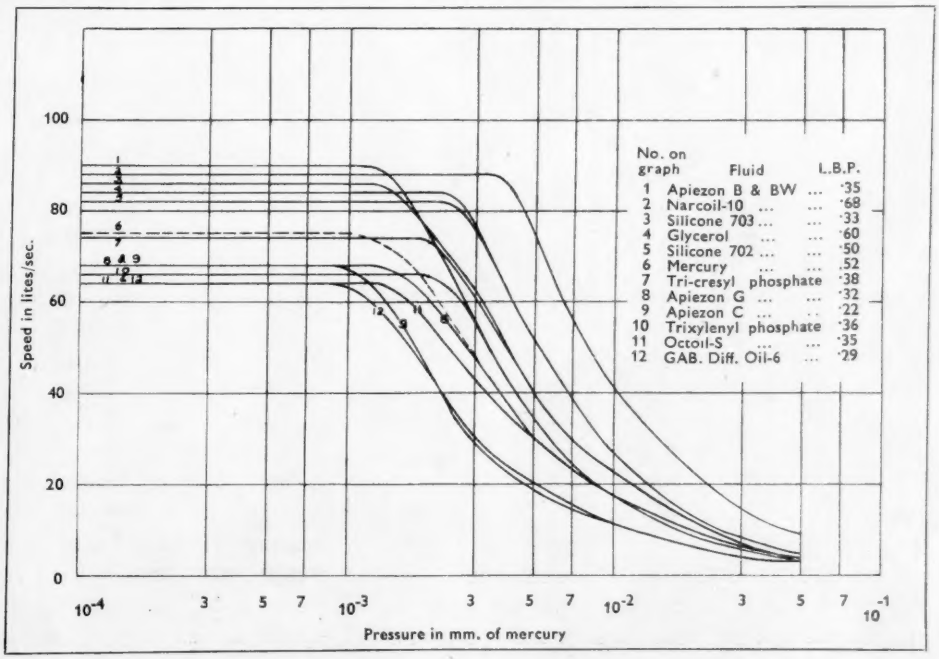

Fig. 4. Speed-pressure curves for various fluids in a 'Speedivac' 203 diffusion pump at 250 watts input and for mercury in a 'Speedivac' 2M2A pump at 350 watts. Insert gives limiting backing pressures (L.B.P.) in each case.

Narcoil 10 to Silicone 703 and Apiezon C the fluids span very wide ranges of molecular weight, boiling point and vapour pressure—yet the differences in the speed curves would be quite unnoticeable in most applications. (We are not now considering behaviour near the ultimate pressure of the pump and fluid where the speed, as measured with the aid of a vapour sensitive gauge, falls to zero.)

The limiting fore pressures—the highest values, the fore pressures can be allowed to reach, if the fine pressures are not to be affected—are tabulated for the various fluids in Fig. 4 and, as would be expected, the more volatile fluids tend to be superior and the more phlegmatic to be inferior in this respect. Thus, if a fluid is particularly good from the point of view of ultimate vacuum, it is probably comparatively bad with regard to limiting fore pressure and *vice versa*, whilst a mixed fluid largely phlegmatic but with a small volatile component will be bad in both respects. The throughput and fore pressure with the most phlegmatic fluids can often be improved by increasing the heater input, but, unless fractionation is good, there is an attendant risk of a deterioration in the ultimate pressure due to increased fluid decomposition (and when such fluids are chosen a very low ultimate is usually desired). These fluids must, of course, run at higher temperatures than those more volatile to achieve the same boiler pressure, so the risk of decomposition is greater as well as being less desirable in their case. 'Backstreaming rate' is also likely to be increased by increasing the heater input (see below).

High throughput and fore pressure are valuable qualities when considerable gas flows or large bursts of gas have to be handled without excessive pressure rise, *e.g.* for evaporating plant, sputtering plant, vacuum furnaces, ovens etc. A high limiting fore pressure reduces the size of the fore pump needed in such cases, and lessens the importance of keeping it and its oil in perfect condition.

(6) Backstreaming

Little reliable information is available about the relative extent to which the various fluids 'backstream', though no comparison of fluid properties would be complete without some mention of backstreaming, particularly because a number of rather misleading statements have been made without adequate experimental evidence. A common fallacy is the supposition that backstreaming is responsible for all the vapour present in the system, whereas vapour is in fact present for *two* reasons.

The condensate on the cooled walls of the diffusion pump (which are normally the coldest region in the system) exerts throughout the system whatever vapour pressure is appropriate to its temperature. There is no mass flow of vapour into the system from this source, and we have the ordinary physical case of an envelope containing a liquid in equilibrium with its vapour, part of the envelope being at a higher temperature than the liquid. Under these conditions the vapour pressure depends on liquid temperature alone and cannot be influenced in any way by baffles. (If some part of the system is colder than the pump walls, there will be a mass flow of vapour from the pump walls to this cold part of the system. This flow also will not be prevented by baffles). Since no vapour flow occurs, this vapour pressure cannot legitimately be attributed to 'backstreaming'.

The two most likely sources of backstreaming vapour are :—

(*a*) The vapour jet itself, from which vapour molecules may back-migrate after collisions with other vapour molecules.

(*b*) Droplets or patches of liquid pump fluid which sometimes collect around the bottom edge of the top jet cap, providing sources for random evaporation. The authors refer to this condition as 'wet running'; it can usually be avoided by careful design.

Vapour from such sources normally produces in the mouth of the pump a concentration of vapour molecules greater than is appropriate to saturation at the temperature of the system walls. The condition is analogous to super-saturation and it persists until the molecules reach the walls of the system; there condensation will generally occur. Thus the function of the baffle normally used above an oil diffusion pump is to limit the region in which 'supersaturation' can occur and so to prevent condensation

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of oil vapour in the system itself.

Condensate on the baffle exerts a vapour pressure corresponding to baffle temperature throughout the whole system, so the baffle should be kept as cold as possible. Although inter-molecular collisions in the baffle are few, the fact that they do occur makes it impossible to design a high speed baffle which completely suppresses backstreaming. It is, therefore, important to keep the rate at which vapour backstreams into the baffle as low as possible.

Backstreaming is influenced greatly by pump design. The length of cooled pump walls above the top jet, the diameter of the jet cap and the design of the whole jet system, the boiler pressure and the degree of fractionation must all affect the backstreaming rate ; and unless, as sometimes happens, a pump runs 'wet' with one fluid and 'dry' with another, or unless the fluid vapour pressures differ greatly, difference in the fluid is likely to matter less than difference in the pump.

The apparatus the authors use to compare backstreaming rates is illustrated in Fig. 5. A slightly tilted copper plate, just above the pump mouth and overlapping it all round, is cooled by the pump cooling water. Condensate collected on the underside of the plate runs down to an extended tongue and drips off the tip. When, after several hours running, a steady drip rate is established a light aluminium cup is moved under the tongue and the drips are collected and counted and subsequently weighed.

The plate appears to catch nearly all the backstreaming vapour, since there is little condensation on the walls of the test header which are also cooled by the same water which cools the plate and pump. This uniformity of temperature ensures that the net condensate collected comes only from the backstreaming vapour. During a test, the drops fall at surprisingly regular intervals and are remarkably uniform in size. The heater input is hand set during measurements and mains fluctuations probably contribute to the slight 'spread' in the results—though it is doubtful whether the backstreaming rate is ever quite constant from day to day.

Some preliminary results presented in Fig. 6 compare the backstreaming rates of the silicones D.C. 702 and D.C. 703 and of Octoil S in a standard $2\frac{1}{4}$ inch bore three-stage pump (Speedivac 203) which runs dry with all three fluids. The pump was pumping an ultimate pressure during each test and a preliminary experiment during which controlled leaks of air were admitted to the header established the backstreaming rate to be independent of pressure at pressures below about 10^{-4}mm. Hg.

The results demonstrate very small differences in backstreaming rate between the three fluids tested—

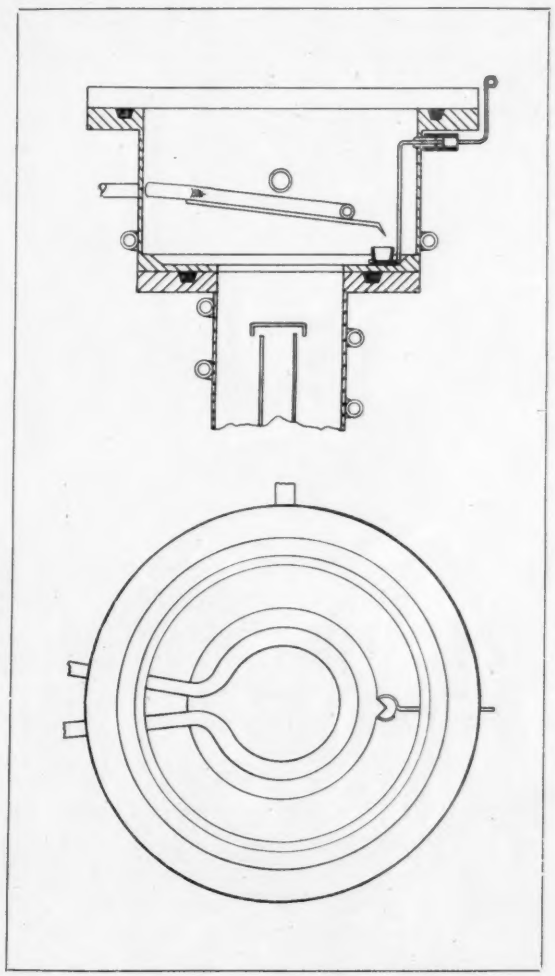

Fig. 5. Apparatus used to measure backstreaming rates.

the selection of heater input being apparently more important than the selection of fluid in this respect.

If collisions between vapour molecules in the vapour jet itself provide, in a 'dry' running pump, the main source of backstreaming, it is perhaps not unreasonable to suggest that the rate of backstreaming measured in molecules per unit time must largely depend on the concentration and temperature of vapour molecules in the vapour jet, and that this concentration must in turn depend mainly on the vapour temperature and pressure in the boiler supplying the jet.

Now, although Octoil S has a somewhat lower vapour pressure than D.C. 703 at room temperature, the vapour pressure-temperature curves published for these fluids by their manufacturers appear to coincide in the region of the normal operating temperature of the pump boiler. Octoil S and D.C. 703 should therefore operate at about the same temperature and pressure in the boiler and the backstreaming rates for these two fluids measured on a molecular basis should roughly coincide.

The similarity of the limiting backing pressures recorded for the two fluids in Fig. 4 confirms that the boiler pressures are sensibly equal at normal input, and the curves in Fig. 6, which cross in the same sense as the vapour pressure-temperature curves for the two fluids, demonstrate how closely the backstreaming rates agree at normal input when measured in molecules/minute.

The curve for D.C. 702 lies only a little above the other two, and indeed no very great difference from the others would be expected if the above arguments are valid. The boiler pressure is somewhat higher with this fluid (compare the limiting backing pressures). But the boiler temperature is, of course, lower.

These arguments can be regarded as no more than suggestions until much more complete experimental evidence has been obtained.

The backstreaming rates presented were measured above the mouth of a high speed non-fractionating pump with a top stage quite near the pump mouth. The provision of a simple one-hit baffle in the mouth of the pump would make the backstreaming rate so small as to be unmeasurable with the apparatus used, and quite negligible for most purposes.

CHOICE OF FLUID

(1) Applications Generally Met by Mercury Pumps

The complete freedom of mercury from decomposition, even at very high boiler pressures (and the possibility of keeping substantially all vapours from the pump out of the system by the use of liquid air) normally dictate the use of a mercury pump in the following cases :—

(*a*) For pumping against very high backing pressures, for example pumps pumping into backing capacities either for gas sampling or for intermittently 'unbacked' pumping, pumps to be backed by factory backing lines or water jet pumps or having a 'barometric leg' in the backing line.

(*b*) For gas handling in gas analysis or gas sampling plant where decomposition products would mingle with the gases being analysed and obscure the results.

(*c*) For making rhodium mirrors by evaporation under vacuum. These seem specially sensitive to vapour contamination, but oil pumps of improved design may yet succeed in this application.

(*d*) For pumping apparatus containing photosensitive or secondary-emission surfaces, or where the characteristics of a primary emitting surface are required to remain constant.

Mercury pumps are also the usual choice :—

(*e*) For evacuating mercury arc rectifiers, mercury vapour lamps or other such apparatus containing mercury—no liquid air trap is required, of course.

(*f*) For pumping chemical vapours which might attack organic fluids.

Mercury pumps are preferred by some workers in some other cases which will be discussed below.

(2) Applications Generally Met by Oil Pumps

The general convenience of oil pumps would

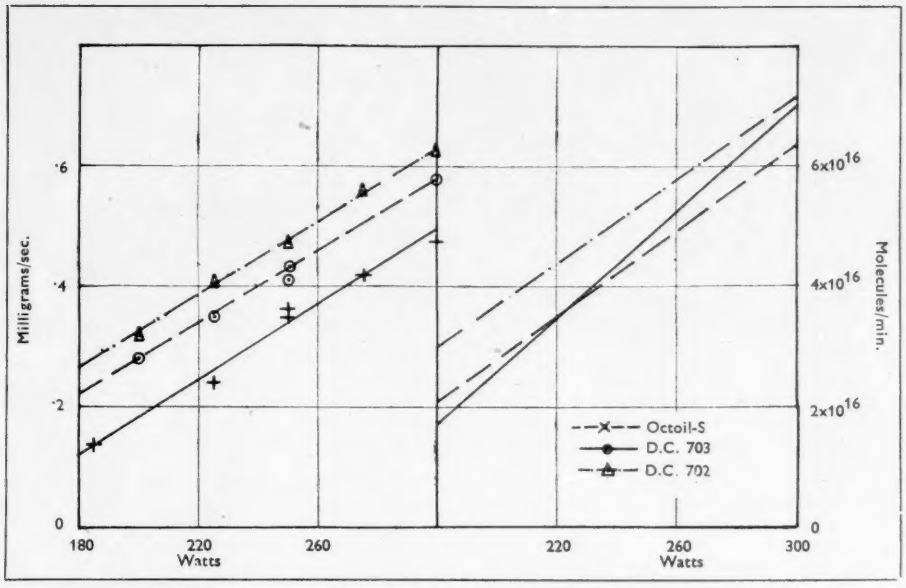

Fig. 6. Backstreaming rates plotted against heater input for a Speedivac 203 pump using various fluids.

suggest their use whenever a strong case cannot be made out for the use of mercury. There are however, no pumping operations completely exclusive to oil pumps. Trapped mercury pumps can always replace them with success at the cost of convenience and economy. However, the following duties would readily be met by oil pumps :—

(*a*) The pumping of all vacuum coating plant, evaporating or (where diffusion pumps are required) sputtering, except in the case of 1(c).

(*b*) The pumping of vacuum furnaces, ovens, melting, casting and sintering plant, degassing plant, etc.

(*c*) The pumping of particle accelerators. However, some cases have been reported where difficulties have arisen due to target contamination by oil vapours.

(*d*) The commercial evacuation of cathode ray tubes and sealed off electronic tubes, generally —except where rotary pumps suffice or where there is a special reason for using mercury pumps.

(*e*) The pumping of high vacuum and molecular stills and fractionating columns.

(*f*) In cases where pumping must continue without any interruption for many days or weeks, it is wise, if possible, to use oil pumps as opposed to mercury with liquid air. In such cases, particularly when a wide short duct connects the mercury pump to the cold trap, it is possible for the loss of mercury from pump to trap to be so severe that the pump is eventually emptied completely of mercury and ceases to function.

A large number of less frequently encountered applications could be added to this list.

(3) Applications Where the Choice is More Difficult

(*a*) *Leak Testing Plant* :—

Commonly used leak testing and leak finding methods—*e.g.*, those employing the balanced Pirani gauge or the palladium ionisation gauge leak detector, depend on the entry of hydrogen through the leak and its detection in the system. The fluctuation in

the rate of evolution of hydrogen from the boiler of an oil pump is one limiting factor in the sensitivity of such devices, (and similarly if CO_2 is used as probe gas). Moreover, even if a gas which is not produced in the pump is used as a probe gas (*e.g.* helium, as is usual with mass spectrometer leak detectors) the ready solubility of gases in cold oil leads to a rather slow clearance of the probe gas from the system after a leak has been found, so that full sensitivity is not immediately recovered. The use of mercury pumps with liquid air traps permits greater sensitivity at some extra inconvenience.

In practice, oil pumps may be chosen for most routine testing, and a plant employing mercury pumps may be reserved for cases where the greatest sensitivity is essential. For example, in one factory palladium window plant using oil pumps sensitive to a leak of 10^{-4} lusecs is in general use, whilst a similar plant employing mercury pumps has been built to provide extra sensitivity where this is specially required, and promises to prove 10 to 100 times more sensitive than the oil plant when suitable amplifiers are available*.

(*b*) *Mass Spectrometers* :—

The danger from the use of oil pumps is similar to that in case (*a*). A range of decomposition products from the pump boiler will be present in the instrument and may obscure the results of an analysis. The ions of mercury are easily recognised and no other contaminant would be expected from a trapped mercury pump. Again, the matter is one of degree, and the concentration of contaminants from a good oil pump may be so low as to be quite negligible in comparison with the sample being analysed. In practice most general purpose mass spectrometers appear so far to be evacuated by mercury pumps, but oil pumps have been used very successfully on instruments intended specially for leak testing. In this connection, C. J. Milner[17] reports much less 'background' in the region of mass 4 when using a silicone pumping fluid than when using a hydrocarbon oil.

*Private Communication from N. Ochert, Research Laboratories, W. Edward & Co. (London), Ltd.

(*c*) *Continuously Pumped Apparatus Containing Emitting Filaments or in Which Discharges Occur* :—

This category includes electron microscopes, diffraction cameras and micro-analysers, demountable X-ray tubes, high speed oscillographs, etc. The employment of untrapped oil pumps on so much commercially available equipment in this category, containing both hot and cold cathodes, indicates that there can be no great disadvantage connected with their use.

Oil vapours undoubtedly affect filament life, particularly in the case of thoriated or coated filaments, also they may decompose and produce local deposits in a discharge or on surfaces subjected to electron bombardment. Such deposits, if insulating, may become charged and cause distortion of an electron beam. These effects can, however, usually be kept sufficiently within bounds to permit the use of oil pumps.

S. G. Ellis* has made some interesting investigations into the sources of contamination formed on surfaces under electron bombardment—which contamination can be extremely troublesome in the class of equipment under discussion. He suggests that vapour from oil diffusion pumps makes only a limited contribution to such contamination. Fore pump oil vapour migrating into the system during rough pumping, gaskets, finger prints and dirt generally make such important contributions that even if liquid nitrogen traps are used above the oil diffusion pumps, or if mercury pumps are used, there may be little or no reduction in the contamination rate. R. L. Stewart[18] has also studied such contamination in a system pumped by a mercury pump with a liquid air trap. He considers it may occur in the presence of the slightest trace of organic vapour and discusses a large number of undesirable effects, it may have.

When designing such apparatus, any filament or discharge should desirably be in part of the system remote from the pump—which should in any case be well baffled. Thoriated or coated filaments are usually best avoided in favour of pure tungsten.

*Private Communication from Dr. S. G. Ellis, Research Laboratories, Radio Corp. of America, Princeton, New Jersey, U.S.A.

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Under these conditions and with a good pump and fluid, untrapped oil pumps seem generally more convenient than mercury pumps and liquid air traps. The use of a high backing pressure mercury pump for an electron microscope or diffraction camera (either alone or as ' backing pump ' for a primary oil diffusion pump) does, however, permit the mechanical pump with its associated vibration and the electric fields of its motor to be switched off for long periods during the taking of pictures.[19]

(*d*) *Some Less Well Substantiated Claims for Mercury Pumps* :—

For the quick obtaining of very low pressures, it is argued that a mercury pump ' conditions '—that is, rids itself of dissolved or absorbed air, moisture, etc. —quicker than does an oil pump. It is also argued that, particularly for systems which are not ideally clean, the high pumping speed of a liquid air trap for contaminating vapours is very valuable.

There is, of course, no reason why a liquid nitrogen trap should not be used with an oil pump; liquid air or oxygen are best avoided because of the risk of explosion if the trap fractures. Cold ' thimbles ', mounted wherever most useful in the system and usually liquid nitrogen cooled, have been extensively used in conjunction with oil pumps.

The authors have no evidence bearing upon the claim that mercury pumps can ' condition ' very rapidly, but they know to their cost how easy it is to contaminate a mercury pump so that it will not ' condition ' at all.

Again it is claimed for mercury pumps that the carry-over of fluid into the backing pump when large quantities of air are drawn through hot diffusion pumps is much less with mercury than with oil. Mercury pumps are certainly being used industrially for the valveless pumping of small electron tubes and of cathode-ray tubes on cycles such that oil pumps would probably experience considerable fluid loss and the claim may be partially conceded. On the other hand, mercury pumps are by no means immune from this sort of loss, which can be extremely severe in certain circumstances—and recently oil pumps have been applied industrially to the valveless pumping of cathode ray tubes, some oil loss being considered a worth while price to pay for the increased convenience.

As an example of what might be expected, the apparatus used to assess the ruggedness of the organic fluids was initially built to investigate the valveless pumping of cathode ray tubes. It demonstrated that 500 ten-inch tubes could be pumped with the loss of 25ml. of D.C. 702 fluid. In practice the loss was somewhat less than this, perhaps because rather longer than 5 minutes was allowed for cooling before roughing down a new tube (the cooling period being occupied with mounting and sealing-on the tube) and perhaps because roughing down through the constricted pumping stem of the cathode-ray tube was slower than in the case of the experiment. It has since been found possible to eliminate about 70% of this loss by employing a suitable trap beyond the backing condenser of the pump—the trapped fluid draining back to the pump. The trap will be described elsewhere. One set of results recorded in Tables 2 and 3 was obtained by its use.

(4) Which Oil to Choose

For general-purpose pumping, the silicone fluids possess a very suitable combination of properties. Pressures low enough for nearly every purpose can be reached, pumps stay clean and free from coke or tar and great liberties may be taken with regard to the admitting of air to hot pumps without serious damage to the fluid. So long as one succeeds in avoiding those accidents or mistakes which would cause the fluid to be carried out of the diffusion pump (or the backing pump oil to enter it), a very long life may be expected from a charge of silicone.

The silicones are also the safest oils to use for valveless pumping to really low pressures—below 10^{-5}mm. Hg ion gauge equivalent in the case of D.C. 702; below 10^{-6}mm. Hg ion gauge equivalent in the case of D.C. 703 in suitable pumps—in cycles where the pumps remain substantially at operating temperature, although other fluids have been thus applied in pumps working with low boiler temperatures.

Aroclor 1254 (of which Narcoil 10 is a highly refined form) can rival the ruggedness of the silicones—

especially since it can be used with a somewhat reduced heater input, but the pressures obtainable are unfortunately too high for some purposes (see Fig. 1). The fluid could be used almost as safely as the silicones for valveless pumping without cooling periods where its ultimate pressure is sufficiently low, and in view of the high throughputs and backing pressures obtainable by its use it is suitable for pumping furnaces, ovens, degassing plant, etc., where very low pressures are not required.

For obtaining the lowest possible pressure, we consider Apiezon C used in a good fractionating pump is somewhat better than the best alternatives. The curves (Fig. 1) would also suggest that there is more chance of winning still lower pressures by better pump design from this fluid than from any of the others, for improved fractionation should tend to straighten out the bottom end of the curve and might also (since the fluid is a mixture and inherently fractionable) result in the whole curve being moved bodily downwards.

Generally speaking other hydrocarbon oils we have tested have no advantages over the silicones and all suffer from the disadvantages of fairly ready decomposition, if exposed to air whilst hot. In certain special cases, however, the different effects in the system of hydrocarbon oil and silicone vapours may influence the choice one way or the other.

Of the esters based on phthalic and sebacic acids, we have tested only Octoil S and its unrefined chemical equivalent. In view of their limited chemical stability these fluids are probably best used in pumps employing moderate boiler temperatures and heater inputs. English practice appears generally to be to use somewhat higher boiler temperatures than does average American practice. The most spectacular claims for Octoil S have referred to the ultimate pressure obtained by its use in a three-boiler glass fractionating pump with carefully controlled heater input. We have no experience of the fluids under these conditions.

Commercial tri-cresyl and tri-xylenyl phosphate were perhaps the most surprising fluids, we tested. They appear to be at least as rugged as the hydrocarbon oils, and, provided fractionation is adequate, they can be used to obtain ultimate pressures which compare with those obtained with the best refined pump oils. The fluids we used were commercial plasticisers and their cost was, of course, considerably less than those of refined pump fluids. We have found nothing to suggest any special difficulties in their use, but our experience is limited and comments of other research workers would be welcomed.

They can, of course, only be used with good results in suitable pumps, and there is the danger that commercial grades will vary from batch to batch.

CONCLUSIONS

For most purposes the differences in pumping speeds, backing pressures and backstreaming rates obtained with the oils mentioned appear to be insignificant. Ultimate vacuum, ruggedness and cost are generally the most important varying factors. For industrial use pressures much less than 10^{-5}mm. Hg are rarely necessary. The choice between a number of fluids giving this order of vacuum may therefore usually be made on the grounds of ruggedness and cost alone. The research worker, however may attach chief importance to the lowest possible ultimate pressure, or the effect of the pumping fluid vapour in his system.

With regard to ruggedness the silicone fluids are outstanding, but somewhat lower ultimate pressures may be obtained with one or two of the purely organic fluids than with the best silicone fluids available. In a very few cases the different effects in the system of the breakdown products of silicone and purely organic vapours may influence the choice one way or the other.

Little positive information is available on the contaminating effects of oils on various types of vacuum systems and it would appear to be very desirable that more of those who have observed such effects should make known their experiences. The authors' experiences with the considerable effects which slight traces of dirt can exert, lead them to suppose that in many cases particular oils have been unjustly blamed. A change in oil is usually accompanied by cleaning the system and a subsequent

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improvement in performance may be due to either operation.

The ultimate vacuum attainable with oils is limited by vapour pressure and by slow decomposition. Oils with lower vapour pressures will only be useful if they are considerably more stable, or if their introduction is accompanied by changes in pump design which reduce the decomposition rate. The pump materials may either react with the oil or catalyse its decomposition and some work is necessary on this subject. The possibility of using very low pressure additives to inhibit decomposition should be investigated.

The low maintenance cost of oil pumps is leading to the consideration of their adoption in certain cases even for the evacuation of apparatus containing mercury, but the use of mercury pumps for gas analysis and high backing pressure applications seems likely to continue indefinitely.

Where extreme surface cleanliness is essential the recent work of Alpert (referred to by A. Von Engel[20]) and others on the absorption of gases by ion gauges may well slowly oust the mercury pumps.

We wish to record our gratitude to Mr. A. S. D. Barrett, Technical Director of W. Edwards & Co., for granting permission to publish this article and also to express our appreciation to Mr. D. J. Crawley for his valuable assistance in the experimental work.

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DETERMINATION OF THE MOLECULAR WEIGHTS of low vapour pressure oils and greases

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Summary

THE CRYOSCOPIC METHOD was chosen, using a graphical method to provide data for calculation. The experimentally determined molecular weights of esters, purified by molecular distillation, gave results which varied only a few per cent. from the theoretical values. Particulars are given of the experimentally determined molecular weights of various low-vapour pressure oils and greases.

Sommaire

LA MÉTHODE cryoscopique a été choisie, utilisant une méthode graphique fournissant les données de calcul. Les poids moléculaires d'esters purifiés par distillation moléculaire, déterminés expérimentalement, donnèrent des résultats différant de quelques pourcents seulement des valeurs théoriques. Des détails sont donnés sur les poids moléculaires, déterminés expérimentalement, de différentes huiles et graisse â faible pression de vapeur.

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INTRODUCTION

IN CONNECTION with the treatment and fractionation of liquids by molecular distillation, it is often found desirable to know the mean molecular weights of the liquids and fractions. Various methods are available based on the principles either of boiling-point elevation, or, alternatively, freezing-point depression. The boiling-point, or ebullioscopic, method employs a special boiler to avoid superheating and requires correction of the boiling-point data to atmospheric pressure. The freezing-point, or cryoscopic, method can be carried out with simple apparatus, adequate quantities of ice being the chief requirement. The cryoscopic method was found to give results sufficiently accurate for the purposes required, and was therefore adopted.

EXPERIMENTAL METHOD

The usual apparatus as described in text books[1] on physical chemistry was used, consisting essentially of a jacketted freezing-point tube with side arm and Beckmann thermometer, the cooling medium consisting of ice and water. 'Analar' benzene, which is readily obtainable, was used as the solvent.

Solid additions were made from a small weighed test tube. Liquid additions were introduced down the side arm by means of the dropper shown in Fig. 1. Alternate manipulations of a finger over the branch A and squeezing the bulb B enable the solute to be first drawn into the receiving chamber, and then ejected drop by drop through the end of the capillary tube into the benzene without touching the sides of the freezing-point tube. The weight of liquid added was obtained by weighing the dropper before and after the addition.

INTERPRETATION OF DATA

When n molecules of solute are dissolved in N molecules of solvent, it may be shown by thermodynamical considerations that, for sufficiently dilute

*M.S. received August, 1952

solutions, the freezing-point depression $\triangle t$ is proportional to the concentration $n/N+n$, that is

$$\triangle t = k\frac{n}{N+n}$$

where k is the cryoscopic constant. From the same considerations, k is given by RT^2/ML where M is the molecular weight, and L is the latent heat of fusion of the solvent, assumed to be constant.

Using literature values, k for benzene is given by

$$\frac{1.99 \times 278.5^2}{78 \times 30.3} = 65.4$$

In practice, k is found to vary a few per cent. from the theoretical value, although, as will be shown later, when using the same apparatus and method, the value of k as experimentally determined remains constant to within about one per cent. for widely different substances.

In order to establish k, the freezing-point depression $\triangle t$ for substances of known molecular weight was required together with a simple and reasonably accurate method of calculating k from the data obtained. This same method should also form the basis for calculating the unknown molecular weights after the value of k has been fixed.

Mair[2] describes a method of calculating the ebullioscopic constant which can also be applied to the cryoscopic constant. The value of k is plotted against molecular concentration, the best line through the points being extrapolated to find k at zero concentration. On trying out this method it was found that the 'leverage' on the line caused by the spread of the plotted points magnified variations in the extrapolated values, and made selection of the most probably correct value difficult.

Brancker, Leach and Daniels[3] suggested a modified equation of the form $\triangle t = k(m)^b$ where m is the concentration and b is a constant having a value near to unity. This equation which was used by Simpson[4] was criticised by Banks[5].

Reynolds[6] recommends a method based on the measurement of the slope of a straight-line plot of $\triangle t$ against the weight of substance added. This method has the merit of simplicity, and it has been adopted for interpreting the work to be described.

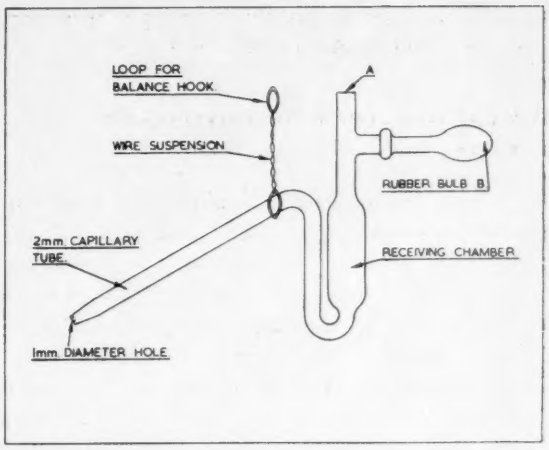

Fig. 1. Dropper for liquid additions. The 1 mm. hole serves to hold up the liquid, except when the drops are ejected.

THEORY

The relation

$$\triangle t = k\frac{n}{N+n}$$

may be expressed as

$$\triangle t = \frac{kM}{Wm}w = \frac{K}{Wm}w$$

where $\triangle t$ is small compared with k; also $K=kM$ and is constant for the same solvent, e.g. benzene.

In this expression, w and W refer to the gm. weights of solute and solvent, and m and M refer to their molecular weights.

Therefore, for dilute solutions, we should obtain a linear plot of $\triangle t$ against w, where K/Wm gives the slope of the line.

Thus

K=cryoscopic constant=slope$\times$Wm

and

m=molecular weight of solute=K/slope$\times$W.

Having established K by means of substances of

known molecular weight, this value of K may then be used to find unknown molecular weights.

DETERMINATION OF CRYOSCOPIC CONSTANT

Low vapour pressure liquids have relatively high molecular weights, which, in general, lie within the range 300 to 800. For purposes of calibration, therefore, it is desirable to include pure chemical compounds of known molecular weight which lie within this range.

Initially, pure naphthalene (analytical standard) was used. As shown in Fig. 2 the points obtained lie on a straight line which passes through the 'zero' reading of the thermometer. From the slope of the line a value of K equal to 5,208 is obtained. A further determination gave a value of K equal to 5,187. The figure of 5,200 may be taken as representing a fair average. It may be of interest to note that this gives a value for

$$k=\frac{5,200}{78}=66.7$$

compared with the theoretical value of 65.4 given previously.

As a check on the value of K derived from naphthalene, various esters generally used as plasticisers were chosen for comparison. Examination of samples of ordinary commercial plasticisers showed that in several cases their values of refractive indices and densities differed appreciably from the published values for the pure substances. It was found that, by subjecting the plasticisers to treatment by molecular distillation, arranged so that the first and last fractions were discarded, the middle fraction gave values of refractive index and density, within the limits of experimental error, similar to those quoted in the literature for the pure substances. The molecular weights of these middle fractions were therefore determined using a value of K=5,200.

The results from three plasticisers treated in this way are given below, straight lines which pass through the 'zero' reading of the thermometer being obtained in each case :—

	Molecular Weights:	
	Theoretical	*Experimentally Determined*
Di-n-Butyl Phthalate	278	276.6
Di-2-Ethylhexyl Phthalate	391	384.3
Di-2-Ethylhexyl Sebacate	426	421.2

A typical plot as obtained for di-ethylhexyl sebacate is shown in Fig. 3.

The fact that all the experimental values given above are less than the corresponding theoretical values suggests that the chosen value of K might be too low. It should be remembered, however, that the molecular weights obtained from cryoscopic data are number averages, and that therefore a small percentage by weight of small molecules has a relatively large effect on the experimental result. For example, one per cent. of a compound of molecular weight 100 in a compound of molecular weight 400 reduces the average molecular weight to about 388. Since the precise degree of purity of the samples tested was not known with certainty, the variation between the theoretical and experimental values does not seem sufficiently great to justify altering the previously selected value of K=5,200.

DISCUSSION OF RESULTS

Although in general the plot of $\triangle t$ against w gave straight lines through the 'zero' readings of the thermometer, it was found in some instances that the points appeared to give lines either of slightly curvilinear shape, or of straight lines which did not pass exactly through the 'zero' point.

In an attempt to obtain further information regarding the relation between the plotted points and various positions of the straight line, a test solution was made up consisting of naphthalene dissolved in a mixture of esters of previously determined molecular weights. The solution consisted of the following :—

	Weight gms.	*Molecular Weight*	
Dibutyl Phthalate	4.312	276.6	As previously determined
Di-Ethyl-Hexyl Phthalate	4.876	384.3	
Di-Ethyl-Hexyl Sebacate	3.603	421.2	
Naphthalene	0.747	128	

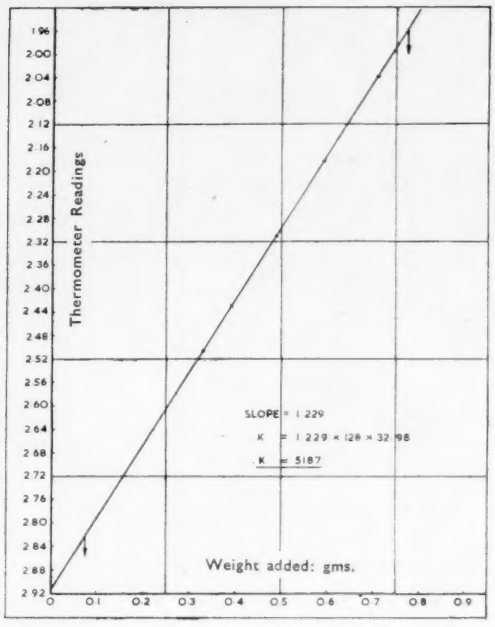

Fig. 2. Plot of Δt vs. w gms. for Naphthalene; the cryoscopic constant K is determined from the slope of the line.

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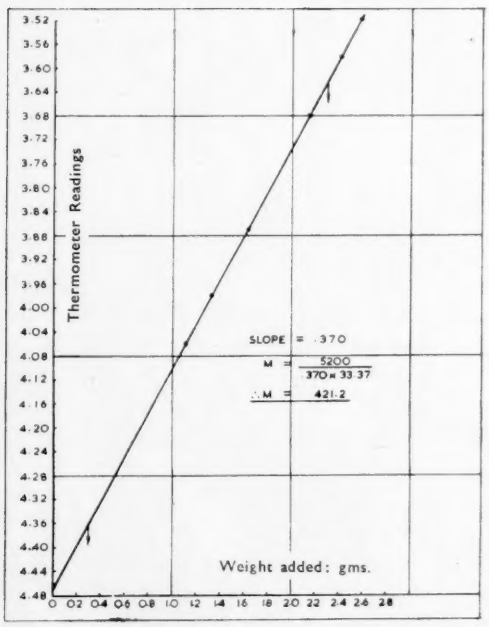

Fig. 3. Plot of Δt vs. w gms. for molecularly-distilled Di-Ethyl Hexyl Sebacate; the molecular weight is determined from the slope of the line.

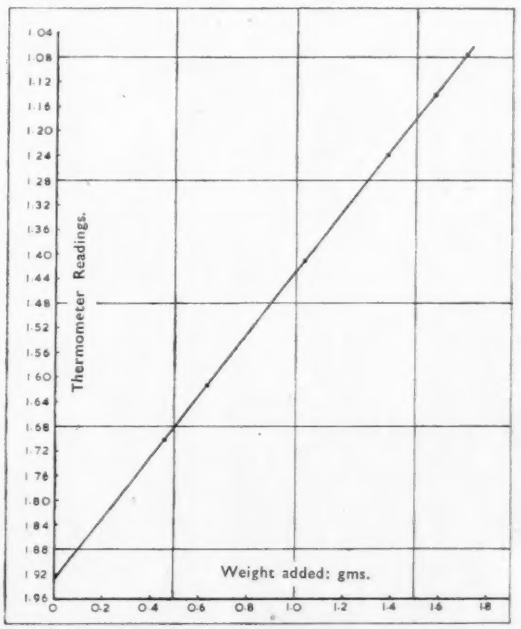

Fig. 4. Plot of Δt vs. w gms. for a mixture of esters and naphthalene in known proportions. The slope of the line gives an average molecular weight comparable with the theoretical value.

totalling 13.538 gms.

The theoretical average molecular weight of the above mixture is given by :—

$$\frac{13.538}{M} = \frac{4.312}{276.6} + \frac{4.876}{384.3} + \frac{3.603}{421.2} + \frac{0.747}{128}$$

whence

$$M = 317.3$$

The results of a series of cryoscopic determinations on this mixture are shown in Fig. 4. The line is drawn through the 'zero' and through as many other points as possible. The slope of the line gives a molecular weight of 314.7, compared with a theoretical value of 317.3 as calculated above.

As both the theory and method are based on the assumption of dilute solutions, those points furthest from the origin are most likely to be in error. For this reason it was decided that the line should be drawn from the zero reading and through, or between, as many other points as possible in proximity to it, least 'weight' being given to those points which lie furthest from the zero.

The foregoing example serves to indicate that the method is satisfactory for the determination of mean molecular weights of low vapour pressure high molecular weight liquid mixtures, and that therefore the method can be applied to mixed hydrocarbons of the 'Apiezon' oil type.

VALUES EXPERIMENTALLY DETERMINED

The following values of molecular weights were obtained using the methods previously described :—

(a) Apiezon Oils

	Molecular Weight
Oil A ..	414
„ B ..	468
„ C ..	574
„ J ..	1,308

(b) Apiezon Water-White Oils

The boiling points[7] at 1 mm. of mercury are added for comparison :—

	Molecular Weight	*Boiling Point at 1 mm.*
Oil FW ..	381	158°C.
„ AW ..	416	176°C.
„ GW ..	453	190°C.
„ BW ..	472	211°C.

(c) Rotary Vacuum Pump Oil

A sample of 'Shell' rotary vacuum pump oil was fractionated in a circulating batch molecular still giving four fractions and a residue :—

	Molecular Weight	*Boiling Point at 1 mm.*
1st Fraction ..	433	195°C.
2nd „ ..	486	216°C.
3rd „ ..	536	231°C.
4th „ ..	567	242°C.
Residue ..	810	267°C.

(d) Silicone Oil

Reliable results could not be obtained from silicone D.C. 200, but silicone D.C. 702 gave a good straight line. The figure for the molecular weight given in Messrs. Dow-Corning's literature is 530 compared with our experimental value of :—

	Molecular Weight
D.C. 702	534

(e) Apiezon Greases

Apiezon M grease and L grease are the residues from the molecular distillation of a special grade of petrolatum, a greater proportion of the lighter fractions being removed in the case of L grease which therefore has the lower vapour pressure. For comparison, the molecular weights of some fractions produced during the processing of L grease are also included.

	Molecular Weight
Apiezon M Grease ..	1,165
Apiezon L Grease ..	
1st Distillate ..	476
2nd „ ..	652
3rd „ ..	1,036
4th „ ..	1,377
Apiezon L Grease (residue)	2,122

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REMARKS

The cryoscopic method as applied to the determination of the molecular weights of low-vapour-pressure organic esters of the plasticiser type, and of petroleum oils and greases, is simple to operate and gives results which are in agreement with the true number-average values, the variation between the theoretical and experimental values not exceeding a few per cent. The interpretation of the experimental results can be readily effected by means of a graphical method chosen to conform to the necessary conditions of dilute solution.

The authors wish to thank Dr. C. Dannatt, M.C., O.B.E., M.I.E.E., Director of Research and Education, and Mr. B. G. Churcher, M.Sc., M.I.E.E., Manager of the Research Department, Metropolitan-Vickers Electrical Co. Ltd., for permission to publish this paper.

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LETTERS TO THE EDITOR

Comments on Catalytic Aluminium Distillation

Sommaire

L'AUTEUR DE CET lettre examine certaines assertions de Docteur Kroll dans son article sur la Métallurgie Sous Vide (Vacuum, Juillet 1951, 163-184).
Réponse de Dr. Kroll à cette critique.

IN HIS PAPER on Vacuum Metallurgy[1] Dr. Kroll confuses two different recent proposals for the production or refining of aluminium.

The first and much more promising of these consists in leading the vapours of certain volatile and stable halides (such as aluminium trichloride), preferably under reduced pressures, *e.g.* 10 mm. Hg over aluminium bearing material, for instance impure aluminium or aluminium alloy, heated to relatively high temperatures, *e.g.* 1,000 °C. By this procedure the vapour of the normally unstable aluminium monohalide is formed which when cooled above the condensation temperature of the applied halide is reconverted into the vapour of the applied halide and metallic aluminium which condenses entirely free from halide. When aluminium chloride is used in this way the reaction is

$$2\ Al + AlCl_3\ (vapour) = 3\ AlCl\ (vapour)$$

Since aluminium chloride sublimes at relatively low temperature it can either be re-circulated as vapour into the system or condensed entirely separately from the aluminium and re-evaporated for further use.

That aluminium monochloride is the product of the reaction was established[2] by the fact that the maximum yield of aluminium obtainable is 2/5th of the weight of the applied aluminium chloride and thus corresponds to the above reaction. Later, the thermodynamics of the process and the conversion (which for practical purposes is very high) have been connected very satisfactorily[3] with the spectrographically known dissociation energy of aluminium monochloride, and have also been firmly established by direct measurements of equilibria involving aluminium monochloride[4].

The second proposal consists in leaching at elevated temperature aluminium bearing material (for instance impure aluminium) with a salt *melt*, preferably consisting of, or containing aluminium chloride, and if so, carried out under pressure. Aluminium thereby dissolves in the melt, from which it is precipitated by cooling and then separated, for example, by filtration. The solubility of aluminium in aluminium trichloride is low ; at 300° to 350 °C (pressure of 10 to 30 atmospheres) it is given as of the order of 1%[5]. The obvious assumption that this solubility is also based on the formation of a lower aluminium halide has not been proven further.

The application of reduced pressure is not absolutely necessary in any of the two processes, but, whereas it is of very great practical advantage in the essential step of the first one, it can be of use in the second only for auxiliary purposes in special cases. If thus, for example, all the salt constituents of the melt have appreciably higher vapour pressures than the monohalide pressure resulting from the reaction between the precipitated aluminium and the halides of the melt, these halides may be separated from the aluminium by evaporating them instead of by filtration.

P. GROSS.

Fulmer Research Institute Ltd.,
Stoke Poges,
Bucks.
14th May, 1952.

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[2] HIGH DUTY ALLOYS LTD. & GROSS, P., *Brit. Pat.* 582,579.

[3] GROSS, P., *U.S. Pat.* 2,470,306 and others.

[4] GROSS, P., CAMPBELL, C. S. KENT, P. J. C. & LEVI, D.L., *Discuss. Faraday Soc.*, No. 4, 1948. 'On Some Equilibria Involving Aluminium Monohalides'.

[5] INTERNATIONAL ALLOYS LTD. & GROSS, P., *Brit. Pat.* 623,932.

Author's Reply. The objections of Mr. Gross are accepted as mostly correct. We should have avoided generalisations such as ' aluminium subhalides ' since the method proposed applied only to one of them, the fluoride, and only when this compound is used in a

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flux. Also the expression 'dissolving' (*page* 176, *second column, line before the last*) should have been explained since it may mean dissolution in a liquid, or in a gaseous medium as well. This appears from the fact, that $AlCl_3$ and AlF_3 sublime (*i.e.* without melting) at 180 and 1,291°C respectively. Both compounds can be stabilised in carrier salts which mixtures, when fused, might well be used to 'dissolve' aluminium scrap as indicated by Mr. Gross, and atmospheric pressure might be used for the fluorides. (See A. Schneider and W. Schmidt, *Z. Metallkunde*, **42**, No. 2, 1951, 43-54). It is evident that in a symposium of the kind presented it would have been impossible to go into more details but a more careful wording might have been possible.

W. J. KROLL.

BOOK REVIEWS

Wolfgang Gaede-Eine Schrift aus dem Nachlass (Wolfgang Gaede—a Paper Printed Posthumously). Edited by DR. M. DUNKEL. (E. Leybold's Nachfolger Cologne, 1951). Pp. 112. Private Print.

In 1950 the well known German firm of E. Leybold & Co., celebrated its hundredth anniversary. As a memento of the occasion Dr. Manfred Dunkel, a director of the firm and a close friend of Wolfgang Gaede, has written this delightful and well produced booklet. The first part is the complete text of Gaede's last important contribution to vacuum physics and technology. In the second half, a brief review is given of the history and development of the firm's activities and a richly deserved tribute is paid to the genius of the late pioneer in vacuum physics and technology, W. Gaede.

In 1905, Gaede designed a new vacuum pump which attracted the attention of Messrs. Leybold, and as a result he was invited to join the firm. From then onwards until his untimely death in 1945 Gaede kept up a continuous association with that firm and all his inventions including his rotary and diffusion pumps were developed and manufactured by Leybold's.

In 1944, Gaede submitted for publication to the Zeitschrift für Technische Physik, the description of a new pump, the 'gasballast' pump suitable for condensable vapours. This article, however, was never published and in 1947 Dr. Dunkel arranged for the publication of an abbreviated version, in which he confined himself to the physical principles of the pump. This article appeared in Zeitschrift für Naturforschung, (1947) 233-8. It is, therefore, a wise choice of the company to commemorate Gaede's long association with Messrs. Leybold by including the complete text of Gaede's last work in the anniversary booklet.

Gaede commences by introducing a new unit of pressure, the 'Ger' named after Otto von Guericke. It is equivalent to 1 cm of water at 4°C and is the technical unit in place of the physical unit. The 'Milliger' differs from the dyne/cm^2 by less than 2% and would equal it if g were taken as 10^3 instead of 981 cm/sec^2. The physical principles of action and the technical details of construction of the 'gasballast' pumps are then described. Finally, the principles involved in vacuum distillation are carefully analysed and the advantages of using the 'gasballast' pump in this connection are clearly discussed.

In conclusion the reviewer wishes to remark that he thoroughly enjoyed reading this booklet. All those interested in vacuum work will find it worth more than a brief glance. It is a pity, it is not readily available. It should be translated into English and published in full.

S. WEINTROUB.

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. . . *of vacuum interest*

Lectures

THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS announce that a national meeting has been arranged to take place from May 11th—14th, 1952, at French Lick Springs Hotel, French Lick, Indiana, U.S.A. The subject of the meeting will be Vacuum Engineering and the following papers will be presented :—

Evaporation Habits of Liquids in Vacuum
Lecturers : *K. Hickman and D. J. Trevoy.*

Rectification at Reduced Pressures.
Lecturers : *H. Bliss, A. M. Eshaya and N. W. Frisch.*

A Survey of Gauges for Measurement of Low Absolute Gas Pressures.
Lecturer : *R. M. Lawrence.*

Outgassing Properties of Materials used in Vacuum Systems
Lecturer : *B. B. Dayton.*

Pressure Drop for High Vacuum Flow of Air Through Annular Sections.
Lecturers : *C. R. Alancraig and L. A. Bromley.*

Problems of the Transport of Vapours Under Residual Gas Pressures Below.
Lecturer : *G. W. Oetjen.*

A New Synoptic Presentation of the Characteristics of High Vacuum Vapour Pumps.
Lecturer : *R. B. Lawrance.*

Selection of Vacuum Pumping Systems.
Lecturer : *L. W. Hull.*

Purification of Vacuum Pump Lubricating and Sealing Oils.
Lecturer : *F. M. Steele.*

Observations on the Design and Operation of High Vacuum Systems.
Lecturers : *C. K. Stoddard and W. E. Mooz.*

Vacuum Facilities for the Study of Supersonic Flow.
Lecturer : *G. J. Maslach.*

Flow Visualisation in High Vacuums.
Lecturer : *R. G. Folson.*

Altitude Test Facilities for Aircraft Engine Research.
Lecturers : *B. R. Leonard and J. N. Viven.*

High Vacuum Technique—The Incurred Savings When Applied to Concentration.
Lecturer : *E. J. Kelly.*

Multi-Stage Ejectors for High Vacuum.
Lecturer : *V. V. Fondrk.*

Corrosion Problems in Steam Jet Vacuum Equipment.
Lecturer : *D. H. Jackson.*

Flash Vaporisation—Analysis of Fluid Mechanical and Mass Transfer Problems and Mass Transfer Problems.
Lecturers : *R. R. Hughes, H. D. Evans and C. V. Sternling.*

Licensable Patents

THE NATIONAL RESEARCH DEVELOPMENT CORPORATION* which is responsible for the exploitation and, where necessary, development of inventions received from the expenditure of public funds (see Volume I, No. 4, page 303) has sent us particulars of two more patents, as follows :—

Patent No. 577,475. *Rotary Pumps.*

The friction normally experienced with the blade against the inside cylindrical wall of Gaede-type pumps is reduced by the use of rolling surfaces. Concentric with the main cylinder a central bush rotates on a ball or roller race ; between the two cylindrical surfaces a series of three or more rollers are in sliding contact. The rollers are driven by an impellor rotating about an eccentric axis. The impellor may take a number of forms in one of which the rollers are accommodated in radial channels in the impellor along which they slide. The impellor forms one end-plate of the pumping chamber and holds the ends of the rollers against the other which is recessed and fixed into the main body. The inlet and outlet are suitably located depending upon the number of rollers. With rotation, the space bounded by the cylindrical wall and the outer edge of the impellor and pairs of rollers varies due to the eccentric movement of the impellor.

Pat. Appln. No. 17061/51. *Cold Traps for Vacuum Systems*

The construction of this cold trap consists of a stack of baffles located inside a pipe or cylinder, which is part of the pumping line. The baffles are cooled by thermal conduction along the central support which is led externally of the pumping line through a suitably lagged vacuum-tight flange into a flask of cooling medium, e.g. liquid air. The baffles can be brazed metal circular dishes bolted to the central support and made easily demountable for cleaning. A conductance of about 48 litres per hour of air can be obtained with a three inch diameter trap over which the pressure can be reduced to less than 10^{-7} mm. of mercury using liquid air as a coolant.

* Enquiries can be addressed to : Dr. B. J. A. Bard, Industrial Manager, The National Research Development Corporation, 1 Tilney Street, London, W.1., England. (Tel. : Grosvenor 5431).

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CLASSIFIED ABSTRACTS

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Vacuum Research, Apparatus and Instruments

The publishers endeavour to make the compilation of abstracts published in this section as comprehensive as possible, but cannot undertake to trace and quote all relevant information published on these subjects.

All abstracts are formulated strictly in accordance with the contents of the original publication, but the publishers are not responsible for such mistakes as may have been made in abstracting. Statements or opinions expressed in the publications quoted do not necessarily represent the experience and/or opinions of the publishers.

Arrangement of Subjects

All abstracts published in this section are allocated to one or more of the subjects shown in the following list:

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13 — ELECTRICAL SCIENCES
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15 — PHYSICS
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(II) Vacuum Apparatus and Auxiliaries

20 — PUMPS
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22 — MEASURING PLANT — VACUUM
23 — INSTRUMENTATION
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(III) Vacuum Processing Techniques

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Three indices are appended to each issue of abstracts: (1) A Cumulative Subject Index in front of the text. (2) a Cumulative Author Index at the back of the text and (3) a List of Periodical Publications quoted. Index (1) and (2) will show all abstracted information published up-to-date in the current volume of the journal.

Filing of Abstracts

All pages containing the text of abstracts are printed on one side only and are detachable ready for filing in special folders. Each main group of subjects (I, II, III, IV) starts on a separate page in each issue and all abstracts in any one group are numbered consecutively throughout all issues of a volume. To distinguish the current numbers of abstracts belonging to one of the four groups from those allocated to other groups, the group number is shown as a suffix to the current number of the abstract *e.g.*, 20/I as distinct from 20/II, etc.

Translations

Translations of some of the foreign publications quoted can be supplied.

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I — General Science and Engineering — I

Abstract No. and References

10 — VACUUM ENGINEERING (GENERAL) — 10

The Services of Vacuum 1/I

United Kingdom. The author surveys the field of vacuum techniques from their inception as a laboratory practice, and subsequent improvements of basic apparatus leading to the industrial applications of to-day. The causes are studied which led to the rapid developments of the last few years and established vacuum processing as a vital requirement for research and industry.

Sommaire: L'auteur fait un exposé du vide sur ses divers aspects.

Article by E. N. da C. Andrade *Vacuum*, 1, Jan. 1951, 3-10

New Trends in Vacuum Research Based on Ionisation Phenomena 2/I

United Kingdom. The range of pressure measurement of the McLeod gauge and the Philips ionisation gauge has been extended recently. For the measurement of ultra-high vacua only the thermionic ionisation gauge can be used, but in such a form that the effect of soft X-rays is reduced considerably. The ionisation gauge also acts as an ionisation pump giving vacua of about 10^{-11}mm. Hg. A method of producing very pure helium gas from liquid helium II is described.

Sommaire : Pour la mesure des vides très poussés, seule la jauge à ionisation thermionique peut être utilisée. La jauge à ionisation agit en pompe à ionisation, donnant des vides d'à peu près 10^{-11}mm.Hg.

Article by A. Von Engel *Vacuum*, 1, Oct. 1951, 257-265

Knudsen Gauges 3/I

See Abstract No. : 15/II

Evaporation from Liquid Surfaces in Vacuum 4/I

See Abstract No. : 49/III

Application of the Mass Spectrometer to High Vacuum Problems 5/I

See Abstract No. : 19/II

The Design of Industrial Vacuum Systems 6/I

United Kingdom. In designing vacuum plant for a given application, close attention should be paid to (1) the right selection of the mechanical components, (2) the provision of electrical power in suitable form and (3) the arrangement of an adequate protective system. The determination of the size and length of the pipes, valves and other elements of the equipment is largely controlled by the laws governing the flow of gases, in particular, the molecular flow. The basic formulae are given. Pipes other than the fine-side connections can be made of welded or solid drawn steel. Light-gauge copper can be used for small pipes. Polythene extruded in lengths convenient for handling and welded into a continuous pipe line on the site could offer economical advantages. The choice of the diffusion pump does not only depend on the volume capacity of the vessel to be evacuated but also on special features connected with the process. To be on the safe side, all pumping speeds arrived at theoretically should be multiplied by a factor of 10. The rotary pump should be capable of roughly exhausting the vessel in the time available for the purpose and of handling the throughput of the diffusion pumps at or below the critical backing pressure, *i.e.*, the pressure, at which the jets of the diffusion pumps break down. The valves should be power-operated, either from a central cam-shaft, or by electro-magnetic action or by compressed air (or hydraulic means). Where power-operation of the valves is provided, it is comparatively easy to introduce centralised control for protective apparatus.

Sommaire : Tous les aspects du montage d'appareillages à vide sont passés en revue et la base théorique des dimensions des canalisations est donnée.

Article by T. S. Millen *J. Sci. Instrum* Suppl. 1, 1951, 7-10

A Bubble Counter for Vacuum Systems 7/I

United States. A bubble counter device is described which facilitates the admission of a measured quantity of gas to an evacuated system at a very low rate of flow. The gas storage container is fitted with a capillary, the bottom end of which projects into the vacuum line. A mercury reservoir is connected with the vacuum system by means of a tube which joins the vacuum line just below the bottom end of the capillary. Two stopcocks in the capillary facilitate proper control of the gas flow. A third stopcock is sealed into the line connecting the vacuum system with the mercury reservoir. This latter stopcock is opened, before gas is admitted, causing the mercury to enter the vacuum line by gravity action and rise to a point just above the

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lower end of the capillary. The gas is now admitted and bubbles through the mercury bath into the vacuum system at a rate which can be measured by counting the number of bubbles per time unit. This arrangement is suitable for flow rates as low as 0.1 cc/cm²/sec.

Sommaire : Description d'un compteur à bulles utilisable en liaison avec l'admission de quantités controlées de gaz dans un système évacué.

Note by W. A. Jenkins *Rev. Sci. Instrum.* **22**, Nov. 1951, 845

Vacuum Techniques—Its Application to Radio and Electronics 8/I

United Kingdom. Modern vacuum machinery employed in the valve industry is discussed. Of the two common types of pumps the rotary pump is extensively used for the evacuation of the ordinary type of receiving valve. These pumps can produce a vacuum of 0.005mm. Hg or better, if a two-stage pump is used or two single-stage pumps are operated in series. Commenting on the diffusion pump the authors enumerate the properties required of a pump fluid. A.o. it must have a low vapour pressure at condenser temperature and good chemical stability at the boiler temperature, even in the presence of air. Mercury was the first fluid used, but as it has a comparatively high vapour pressure, approx. 3 micron Hg at room temperature, elaborate means of refrigeration were required, for the evacuation of cathode ray tubes for instance. In 1928 it was discovered that certain highly refined mineral oils could be used as pump fluids and would give vacua of the order of 10^{-3} micron Hg without refrigeration, but these oils lacked thermal stability and therefore oil diffusion pumps were not popular in that industry until silicone oils became available. The authors proceed to discuss all types of vacuum gauges and methods of leak detection. Using the Pirani gauge as the detector element and hydrogen as a tracer gas, leaks can be detected of a minimum size of 0.1 lusec. The mass spectrometer method facilitates the detection of still smaller leaks and the palladium window ion gauge can trace leaks of the order of 10^{-4} lusec. Discussing production arrangements for the manufacture of valves the authors mention the circular table and the in-line exhaust machine. Sketches of both types of machines are given. In some instances circular tables are in operation, where valves undergo complete pumping and final processing in two to three minutes, one valve being completed every five seconds. In conclusion, the authors refer to the latest developments in vacuum coating techniques, vacuum impregnation procedures and resistor manufacture.

Sommaire : Discussion des développements récents d'appareils à vide nécessaires à l'industrie électronique.

Article by D. Latham & B. D. Power *J. Brit. I.R.E.*, **11**, Dec. 1951, 561-568

The Production, Properties and Uses of Thin Films Condensed In Vacuo 9/I

See Abstract No. : 1/III

Vacuum Deposition 10/I

United Kingdom. Industrial applications of vacuum coating techniques are reviewed, in particular, metallisation. In most cases the costs per unit are lower than in the case of other forms of processing. Due to the small amount of metal required current government regulations restricting the use of certain materials do not apply. The process is clean; there are no fumes, splashing liquids or corrosive baths. The metallising process consists of four major steps : cleaning of the surface to be metallised, application of an undercoat, deposition of the metal and application of a top coat. Cleaning is usually effected by bombarding the surface with ions. The cleaning of glass objects by electron bombardment is mentioned. The undercoat (lacquer) seals the pores of the surface and at the same time prepares the surface for the desired finish of the metal deposit (bright finish, wrinkle finish, etc.). The top coat (lacquer) is applied to prevent abrasion of the thin metal film. Details of the production procedure are given.

Sommaire : Revue des procédés de métallisation par évaporation sous vide.

Article by Anon. *Prod. Finish.* **4**, Dec. 1951, 52-56

High Vacuum Metallising of Metals and Plastics 11/I

See Abstract No. : 4/III

' Evaporation Coating ' Leathers 12/I

United States. The uses of vacuum coating techniques in the leather industry are discussed. Several applications are mentioned, for instance : the manufacture of heat-insulated leather clothing for wear in extremely cold weather. Jackets made from leather and fabric material embodying a thin aluminium layer as an interliner retain their flexibility and light weight and reflect the body-heat without reducing the ' breathing ' quality of the fabric. Fancy ballroom slippers or other leather goods can be coated by these techniques with advantage where it is important not to obscure the leather grain effects. The material to be deposited is preferably gold or aluminium. Details of the production procedure are given.

Sommaire : Discussion des techniques de revêtement sous vide pour l'industrie du cuir. Des couches d'aluminium employées comme doublures intérmédiaires constituent des isolants conservant la chaleur du corps humain dans les vêtements destinés aux températures extremement froides.

Article by T. A. Dickinson *Leather & Shoes* **122**, 25.8.51. 8, 33 & 34.

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A Review of Laboratory Freeze Drying with Particular Reference to Viruses 13/I
See Abstract No. : 13/IV

Freeze Drying—Vacuum Sublimation 14/I
See Abstract No. : 14/IV

Symposium on Freezing and Drying 15/I
See Abstract No. : 15/IV

Training in Vacuum Technology 16/I

United Kingdom. The author discusses the subject of training for vacuum work and suggests that there is a need for special courses for post-graduates or technicians who have completed their basic training. The Northampton Polytechnic, with which the author is associated, has arranged for a course on vacuum technique as a permanent feature of its educational programme and the author gives a detailed description of the syllabus of the course, the laboratory facilities available and the practical work included in the course.

Sommaire : L'auteur discute le sujet de l'education du personnel chargé des travaux de vide et suggère des cours spéciaux pour ingénieurs et téchnicians ayant terminé leurs autres études.

Article by F. Y. Poynton *Vacuum*, 1, April 1951, 92-96

13 — ELECTRICAL SCIENCES — 13

Noble Gas Hot-Cathode Diodes with Negative Arc Drop 17/I
See Abstract No. : 18/IV

A Study of Rectification Effects at Surfaces of Germanium and Lead Sulphide 18/I

United Kingdom. In a previous investigation the authors dealt with the adverse results that polishing of the surfaces of germanium and lead sulphide specimens has on the point-contact thermo-electric effects. They found that this condition can be counteracted by chemical etching of the surfaces and heat treatment *in vacuo*. In the present work the authors investigate the effects of similar treatment on the rectification characteristics of germanium and lead sulphide crystals. The probe contact manipulator described in the previous publication has been employed again for the investigation of the diode properties of the various germanium and lead sulphide surfaces. Measurements of the peak back voltage served as a criterion for the rectifying performance. The heat treatment was carried out in an all-glass vacuum system at a pressure of 10^{-4} to 10^{-5}mm. Hg. Two different heat treatment procedures were employed. In the first case the heating period was 1½ hours at 200°C, following which the germanium specimen was removed from the furnace for examination. This cycle was repeated at 400, 600, 800 and 900°C. In the second case the heat treatment was carried out at a constant temperature (500°C), but the period of each treatment was varied and the specimen allowed to cool down between two heating periods. It is known that thin germanium films deposited by vacuum evaporation on etched germanium substrates produce marked changes in the photovoltaic and thermo-electric properties. The same procedure was applied here and its effects on the rectification properties were examined. The authors came to the conclusion that polishing of the crystals produces an amorphous surface layer. This layer can be removed successfully either by chemical etching or by thermal treatment *in vacuo*. Depositing a thin germanium film on to a cold etched germanium surface results in a top layer of similar properties. Removal of this amorphous layer by recrystallisation may be preferable to removal by chemical etching.

Sommaire : On étudie la structure des surfaces régissant les conditions de rectification des films de germanium et l'on discute le résultat d'expériences sur le traitement à chaud sous vide.

Article by C. A. Hogarth & J. W. Granville *Proc. Phys. Soc.*, **64B**, Nov. 1951, 992-998

Electrical Properties of Thin Layers of Germanium 19/I

France : Layers of germanium about 1 μ thick were deposited by vaporisation *in vacuo* at 1,400° from a corundum crucible, on to a quartz or molybdenum support. The electrical resistance and rectifying properties were determined. If the support was above 370° the resistance was about 0.025 ohm/cm; if below 270°, it was about 10 ohm/cm; for intermediate temperatures the results were not well reproducible. In accordance with the work of König the germanium deposited at low temperatures was amorphous, that deposited at high temperatures was crystalline. Similar results were obtained if the germanium was deposited on a cold support and heated afterwards. The rectifying action on 50-cycle a.c. was studied with a circuit that allowed the determination of the resistance with a continuous current, rectified current in a short circuit, and rectified potential in an open circuit. Amorphous germanium gave small rectified currents in a short circuit and high potentials in an open circuit; the opposite was true of crystalline germanium. A ' complex ' layer of germanium

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was obtained by depositing first a thick crystalline layer on a support heated to 400°, then a thin amorphous layer at room temperature. Much greater rectified power could be obtained with this.

(*Chemical Abstracts*)

Sommaire : On a déterminé la résistance électrique et les propriétés rectificatives des couches de germanium d épaisseur 1 μ déposées par évaporation sous vide à 1,400°, et l'on a étudié les facteurs affectant leur performance.

Article by J. M. Dunoyer *J. Phys. Radium*, **12**, 1951, 602-606

Vacuum Drying of Electrical Insulation in the Service Shop

See Abstract No. : 34/III

20/I

15 — PHYSICS — 15

An Introduction to High Vacua in Nuclear Physics

21/I

United Kingdom. The need for high vacua in the study of nuclear physics and the consequent parallel development of these subjects is outlined. The nature of nuclear reactions and the vacuum requirements of associated instruments is then described.

Sommaire : L auteur exposé le developpement qu'a pris la technique du haut vide parallèlement avec l'étude de la physique nucleaire, laquelle en est tributaire.

Article by A. S. Baxter *Vacuum*, 1, July 1951, 185-190

A Liquid Hydrogen Target

See Abstract No. : 65/III

22/I

Vacuum-Powder Insulation for Low Temperatures

23/I

United Kingdom. A review is given of the development of vacuum-powder insulation, from the early experiments of Smoluchowski and Dewar to the present day and the importance of thermal insulation at very low temperatures is explained and emphasised. The theory of thermal conduction of porous materials is then briefly considered in terms of the variables involved, with particular reference to pressure. Recent experiments at low temperatures on four typical insulants over a pressure range of 760 mm. to 0.001 mm. Hg are described and the results correlated theoretically. A brief outline is given of industrial applications of the method, and substantial developments in the future are envisaged.

Sommaire : Un compte rendu du développement de l'isolement par poudre vide depuis les premiers travaux de Smoluchowski et Dewar. Des expériences récentes à basses températures, sur quatre isolants typiques sur une gamme de pression allant de 760 mm. à 0.001 mm. Hg sont décrites et les résultats comparés théoriquement.

Article by L. L. Katan *Vacuum*, 1, July 1951, 191-202

Multiple-Beam Interferometry and the Influence of Vacuum Technique

24/I

United Kingdom. A discussion of the influence of specific vacuum techniques on the preparation of the highly reflecting thin films used for multiple-beam interferometry. It is shown that the absorption of the film plays an important part particularly with reflection type fringes and that it should be as low as possible. The factors affecting absorption are surveyed. It is concluded that good films are produced by evaporation of silver using a mercury diffusion pumping system with an efficient liquid air trap. Oil (or silicone) diffusion pumping systems without traps can produce films of high reflectivity but the absorptions of such films are greater than those using the mercury pump with trap. Cleaning techniques and empiric methods for assessing the films formed are described in detail. Silver is the best metal so far available for multiple-beam interferometry.

Sommaire : Discussion d l'influence des techniques du vide particulières sur la préparation des couches minces à haut pouvoir réflecteur utilisées pour l'interferométrie à rayons multiples.

Article by S. Tolansky *Vacuum*, 1, April 1952, 75-91

The Effect of Phase Changes in White Light Interferometry

25/I

United States. The author investigated the effects of phase changes on the accuracy of multiple beam interferometry methods where monochromatic light is reflected from the surfaces of a variety of evaporated metal films. Two materials in particular have been investigated, silver and aluminium. In one series of experiments filters employing MgF_2 as the dielectric have been used and in the other filters employing air as the dielectric. The author comes to the conclusion that the phase varies with the wavelength of the light, and that it is necessary to provide for proper corrections if accurate results are to be expected from the Tolansky method of determining film thickness.

Sommaire : L'auteur examine la question s'il est permis de ne pas tenir compte des effets de changement de phase de la lumière blanche dans le procédé de mesure de l'épaisseur de couche minces par la méthode de Tolansky.

Article by L. G. Schulz *J. Opt. Soc. Amer.* **41**, April 1951, 261-264

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The Refraction Index of Thin Al_2O_3 Films 26/I

See Abstract No. : 26/III

Surface Treatment of Lenses 27 I

See Abstract No. : 8/III

On the Production of Diffraction Grating. I. The Copying of Plane Gratings 28/I

United Kingdom. The making of accurate diffraction gratings is one of the most difficult tasks called for by the physicists and the number of specialists available for the production of such gratings is much too small considering the demand. The author examined the possibility of developing a process which requires less individual skill. The conventional method consists of three principal stages : (1) a helix is cut upon one half of a polished metal cylinder having a pitch equal to that of the required grating, (2) the helix is copied on to the other half of the cylinder in such a manner that the periodic errors of the first helix are corrected, (3) the corrected helix is transferred to a flat surface by means of Merton's replica process. The author deals with stage no. 3 only and investigates the difficulties inherent in the conventional process. An improved method is suggested for the production of the replica which, as a final step, is aluminised by evaporation *in vacuo*. The accuracy of the improved procedure is demonstrated by interferograms attached to the article.

Article by G. D. Dew & L. A. Sayce *Proc. Roy. Soc.* **A207**, 22.6.1951, 278-284

Sommaire : On donne les details d'une technique pour la production de reseaux de diffraction optique, où l'emploi d'alumine déposé par évaporation est un facteur important de la production.

Density Control in the Manufacture of Rhodium Filters 29/I

See Abstract No. : 9/III

Photo-Electric Cathodes of the Lithium-Antimony Type 30/I

France. The performance of photo-electric cathodes of the lithium-antimony type has been studied. The thermionic emission of these cathodes has been found to be comparatively weak. It appears that these cathodes can be used with advantage for investigations in the violet and ultra-violet region. Their performance in that region appears to be superior to that of caesium-antimony cathodes.

Article by N. Schaetti & W. Baumgartner *Le Vide*, 6, July-Sept. 1951, 1041-1045

Sommaire : Détails de recherche portant sur les cathodes photo-électriques du type lithium-antimoine.

A Photo-Conductive Effect in Tellurium Films 31/I

United Kingdom. Measuring the resistance of thin tellurium films it was noticed that the resistivity of the films decreased when exposed to sunlight. Investigating this phenomenon further the films were placed in a box which was closed and their resistance measured some time afterwards. Then the lid of the box was lifted and sunlight admitted. Measurements taken during the first 15-60 minutes after opening the box showed that the resistance of the films dropped rapidly during the initial period of exposure and finally reached a steady value which is about two-thirds of the resistance value obtained before sunlight was admitted. When the lid of the box was closed again, the films recovered their resistance value after about one day in darkness. It is suggested that this effect could be used with advantage in photo-cells which are not intended to react to rapid fluctuations of illumination. The tellurium films used in this experiment were deposited on glass *in vacuo* and had a thickness of 3×10^{-6}cm. Several films were tested, but it was found that the speed of response differed, even where the films tested had been deposited simultaneously.

Letter by W. T. Blackband *Nature* **168**, 20.10.51, 704

Sommaire : Des films de tellure, placés dans une boîte à l'abri de la lumière du jour présentèrent une resistivité électrique plus élevée qu'après exposition au jour. Après fermeture de la boîte, les films reprirent leur resistivité initiale.

Photo-Conductivity in Vacuum-Coated Selenium Films 32/I

See Abstract No. : 15/III

Contamination of Evaporated Films by the Supporting Material of the Source 33/I

United Kingdom. Studying the properties of evaporated films it is important to know, whether the deposit is contaminated by the material of the evaporation source. The author employed a radio-active tracer method which is sufficiently sensitive to indicate contamination, if present. Tantalum has an active isotope, tantalum-182. Since the whole of natural tantalum consists of the isotope-181, from which the radio-active isotope is produced, a high specific radio-activity can be obtained easily. The author deposited silver and germanium films using an active tantalum boat as the crucible and found that the tantalum content of the germanium

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film was 11 p.p.m. for an evaporation temperature of 1,120°C and 26 p.p.m. for an evaporation temperature of 1,800°C. The corresponding figures for the silver film were 20 p.p.m. and 113 p.p.m. No satisfactory explanation can yet be given on how the tantalum is transported.

Sommaire : Des essais ont été faits pour établir l'avantage de traceurs radio-actifs pour la détermination de la contamination de films évaporés par la matière du creuset.

Letter by O. S. Heavens *Nature*, **168**, 13.10.51, 664

Research on Electronic Valves Assisted by Radio-Active Materials 34/I

See Abstract No. : 27/IV

A Microilluminator for the Study of the Infrared Spectra of Small Samples at Low Temperatures 35/I

United States. The instrument described combines the functions of two devices: that of a reflecting microscope used in conjunction with a spectrometer to obtain infrared spectra on extremely small samples, and that of a special absorption cell which can be used to obtain the infrared spectra of solids at low temperatures. The optical system is placed in a cylindrical case with four outlets. One outlet serves as a connection to the vacuum system and another as support for the Dewar vessel carrying the sample holder. At the front and rear the housing is closed by plates which carry appropriate infrared transmitting windows. The instrument has been designed primarily for use with the Beckman I.R.2 spectrometer and for insertion in a parallel beam. The linear magnification obtained in connection with the I.R.2 is about 18 and the numerical aperture approximately 0.56. With optimum adjustment in the light path of the Beckman the microscope transmits approximately 40% of the radiation available. The sample holder tended to be displaced during cooling, therefore the Dewar vessel has been joined to the housing by means of a bellows. This facilitates accurate location of the specimen at the optical focus. It takes five minutes to cool the specimen down to -185°C. To reach this temperature 50 ml. of liquid nitrogen are required and to maintain it, 40 ml./hr. are needed. It is important to have efficient vacuum pumps to avoid the formation of ice on the specimen. The instrument is connected to a silicone oil diffusion pump which ensures the maintenance of a pressure of 2×10^{-5}mm. Hg and prevents serious ice formation during the first hour after cooling.

Sommaire : Description d'un micro-illuminateur pour l'étude des spectres infrarouges de petite specimens; cet appareil joue le double rôle de microscope réfleteur et de cellule spéciale d'absorption qui peut être évacuée et refroidie à de basses températures.

Article by R. M. Badger & R. Newman *Rev. Sci. Instrum* **22**, Dec. 1951, 935-936

Flow of Gases and Vapours in a Porous Medium and its Bearing on Adsorption Problems. I. The Steady State of Flow 36/I

United Kingdom. A study has been made of the steady state of flow of He, Ne, A, Kr, H_2 O_2, N_2, NH_3, CCl_4 and SO_2 through a bed of small, nearly spherical, synthetic analcite crystals. Flow rates, permeabilities, Knudsen and Poiseuille contributions to permeability, and permeability constants have been determined and used to test the applicability of several equations of flow. Significant deviations from the behaviour suggested by these equations have been observed, especially for vapours. Pore properties and total surfaces have been determined using procedures based on steady state flow data.

(*Science Abstracts*)

Sommaire : Flux de gaz et vapeurs dans matériaux poreux et leur influence sur les problèmes d'adsorption. (I : l'état fixe du flux).

Article by R. M. Barrer & D. M. Grove *Trans. Faraday Soc.*, **47**, Aug. 1951, 826-837

Flow of Gases and Vapours in a Porous Medium and Its Bearing on Adsorption Problems. II. Transient Flow 37/I

United Kingdom. By measuring the time-lag L in setting up the steady state of flow one may measure the diffusion coefficients of gases in a porous medium and obtain a mean pore radius and an internal surface of the porous medium independently of all steady state methods. In beds of analcite crystals the inert gases, permanent gases and CCl_4 behave as though they were not adsorbed appreciably at low pressures while ammonia and sulphur dioxide show strong adsorption effects. In very dilute adsorbed films of NH_3 and SO_2 surface diffusion, while not necessarily absent, is limited in extent. The lifetimes τ of molecules in the adsorbed states are then given by the equations : $NH_3 : \tau = 3.1 \times 10^{-11}$ exp (4 300/RT) sec. $SO_2 : \tau = 6.6 \times 10^{-11}$ exp (3 010/RT) sec.

(*Science Abstracts*)

Sommaire : Flux de gaz et vapeurs dans matériaux poreux et leur influence sur les problèmes d'adsorption. (II : flux transitoire.)

Article by R. M. Barrer & D. M. Grove *Trans. Faraday Soc.*, **47**, Aug. 1951, 837-844

Surface Area Measurements by the High Vacuum Nitrogen Adsorption Method 38/I

United Kingdom. Details are given of the design factors of an improved apparatus for the determination of the surface area of finally divided materials by the Emmett method. Results achieved with the improved apparatus are discussed and various examples quoted.

Sommaire : Description des modifications de construction apportées à un appareil pour la détermination de l'aire de surface de matériaux par la méthode d'Emmitt et discussion des caractéristiques de l'appareil.

Abstract of a Lecture by C. T. M. Smith *Chem. & Industr.*, 24.11.51, 1034

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16 — CHEMISTRY — 16

Determination of the Molecular Weights of Low Vapour Pressure Oils and Greases — 39/I

United Kingdom. The cryoscopic method was chosen, using a graphical method to provide data for calculation. The experimentally determined molecular weights of esters, purified by molecular distillation, gave results which varied only a few per cent. from the theoretical values. Particulars are given of the experimentally determined molecular weights of various low-vapour pressure oils and greases.

Sommaire : Des détails sont donnés sur les poids moléculaires, déterminés expérimentalement, de différentes huiles et graisse à faible pression de vapeur. La méthode cryoscopique a été choisie utilisant une méthode graphique fournissant les données de calcul.

Article by G. Burrows & R. Jackson *Vacuum*, **2**, Jan. 1952 50-55

Apparatus for the Microdetermination of Molecular Weights of Volatile Liquids — 40/I

United States. The apparatus for the microdetermination of molecular weights of volatilisable liquids described here represents an improvement over the method proposed by Young and Taylor. It eliminates the necessity of manipulating in a high vacuum. The new apparatus is fitted with a click gauge to indicate when a certain defined pressure difference exists between an external manometer system and a test cell. The apparatus consists of a ' U '-shaped piece of glass tubing, one arm of which ends in a sintered glass disc sealed-in near the bottom. The clicking membrane is fitted to the other arm at about the same level. This bottom section of the ' U ' forms the test cell. The arm incorporating the clicking membrane carries a ' T '-piece connecting the manometer, a water jet pump, a stopcock for the controlled admission of air and the arm of the test cell carrying the sintered glass disc by rubber tubing when required. In operation, the whole system is heated up to the desired temperature by immersing it in a beaker filled with a mineral oil. Subsequently, connection is made between the arm carrying the disc and the water jet pump, and the cell is evacuated to a pressure of 3 cm. Hg. Then, the rubber tubing is removed and air admitted to the arm carrying the click gauge. When the click is heard, the stopcock is closed and the first manometer reading taken. At this stage the sample is introduced by means of a specially designed pipette and, when temperature equilibrium has been established in the test cell, air is again admitted into the arm carrying the click gauge until a click is heard. Now a second pressure reading is taken completing the determination. The formula for calculating the molecular weights is given.

Sommaire : Description d'un appareil pour la microdetermination des poids moléculaires des liquides volatilisables. L'appareil constitue un perfectionnement de la méthode Young et Taylor et comprend une jauge de clic pour les mesurages des pressions.

Article by L. K. Nash *Analyt. Chem.*, **23**, Dec. 1951, 1868-1870

On the Accurate Determination of Vapour Densities and Molecular Weights — 41/I

Belgium. An experimental procedure is described which facilitates the accurate determination of vapour densities. Details of the method of calculating the molecular weights from these measurements are given. This method is correct even for vapours which are weakly associated.

Sommaire : Description d'une méthode expérimentale pour la détermination des densités de vapeur. On donne des détails d'une méthode pour le calcul des poids moléculaires basée sur ces mesurages des densités de vapeur.

Article by W. Mund & R. Coekelbergs *Bull. Classe Sci.* 1951, 146-154

Latent Heats of Vaporisation of Some Organic Compounds — 42/I

United States. Knowledge of the latent heat of vaporisation applicable is necessary whenever it becomes desirable to evaluate a heat effect which is due to the transfer of a material from the liquid to the vapour phase or *vice versa*. Such values are available only for a few compounds in pressure regions other than atmospheric. The article refers to a table which has been compiled recently giving the latent heats of vaporisation of 88 organic compounds covering the range from 1 mm. Hg to the critical pressure in each case. The values incorporated in the table have been calculated by using the formula :—

$$\Delta H = \frac{2.3026 \quad RBT^2}{M\,(t + C)^2} \quad \sqrt{1 - \frac{T_c^3}{P_c} \quad \frac{P}{T^3}}$$

Where ΔH is the latent heat of vaporisation, B and C constants. The formula is a combination of Clapeyron's equation for the calculation of latent heats, the differentiation of Antoine's equation for the evaluation of the rate of change of vapour pressure with temperature and Haggenmacher's equation for the expression of the difference between the specific volume of saturated vapour and the specific volume of saturated liquid. The table is on file at the American Documentation Institute.

Sommaire : Une table donnant les points de chaleur latents de vaporisation pour 88 matériaux composés organiques et couvrant une gamme allante de 1mm. Hg à la pression critique dans chaque cas. On indique le détail des procédés employés pour arriver à ces valeurs.

Article by J. B. O'Hara & R. W. Fahien *Industr. Engng. Chem.*, **43**, Dec. 1951, 2924-2925

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A Spinning Band Column for Vacuum Fractionation of Fatty-Acid Esters — 44/I

See Abstract No. : 54/III

A Modified Spinning Band Column for Low Pressure Fractionation — 45/I

See Abstract No. : 53/III

Process Control by Mass Spectrometer — 46/I

United States. Process monitoring by means of a mass spectrometer has recently been arranged for at the gas plant of an oil company, to check continuously on the composition of the bottom stream from a de-ethaniser distillation column. The conventional analytical procedure of collecting samples periodically used to take 24 hours before differences from the required composition were discovered. In theory, mass spectrometer monitoring should reduce the time lag to 20 seconds. In practice, the time required is six minutes. Details are given of the operation of the instrument. The sample is taken from the stream through a needle valve, a total of 0.4 cm^3/minute is required for the analysis. A self-standardising system is installed to ensure high accuracy by compensating automatically for small changes in sensitivity. The monitoring type of mass spectrometer differs from the original type by proceeding analytically in a stepwise fashion from one to the next of a limited number of pre-selected mass peaks, instead of continuously scanning a relatively extended region of the mass spectrum.

Sommaire : Description des performances d'un spectromètre de masse utilisé comme un instrument monitoire en rapport avec une application dans une raffinerie de pétrole.

Article by C. F. Robinson *Chem. Engng.*, 58, Dec. 1951, 136-137

Modern Analytical Distillation of Crude Petroleum — 47/I

See Abstract No. : 55/III

Vacuum Flash Evaporator Removes Volatiles from Oils — 48/I

See Abstract No. : 33/III

Activated Adsorption of Hydrogen on Nickel Catalysts — 49/I

Holland. The thermo-dynamics and kinetics of the chemisorption of hydrogen on metals are of considerable importance as a guide in the exploration of the mechanism of hydrogenation reactions catalysed by these metals. The authors refer to the experiments carried out by O. Beeck *et al.* who worked with thin metal films such as nickel, and the work of A. F. Benton *et al.* who worked with reduced nickel compounds. The former group of research workers found that the adsorption velocity of hydrogen is extremely rapid except for a small amount which is adsorbed at a slow and measurable rate. If the temperature of adsorption is increased the total adsorption is considerably decreased but the amount of hydrogen adsorbed slowly is still the same. The latter group of research workers found that a certain part of the adsorption is fairly rapid but stated that a considerable amount of hydrogen is adsorbed slowly. Furthermore, they found that the amount adsorbed increases as the temperature increases and this led to the conception of ' activated ' adsorption. The authors of the letter experimented with a catalyst consisting of 100 parts of nickel to 29 parts of silica (by weight) obtained by co-precipitation from nickel nitrate, sodium carbonate and sodium silicate solutions and subsequent reduction. They observed that both types of behaviour can be reproduced. The all-important parameter proved to be the temperature of the reduction. Where reduction took place below 400°C, the sample obtained was comparable in behaviour to those described by the Benton group. If, however, the temperature was higher than 500°C, the behaviour was similar to that found by the Beeck group. In addition, the authors found that in the case of the catalyst used in their experiment reduction was incomplete below 400°C but substantially complete above 500°C. This seems to indicate that the oxygen content of the metal obtained is responsible for the ' activated ' adsorption. J. K. Roberts claimed that ' activated ' adsorption is due to part of the surface being covered by oxygen. The experiments of the authors appear to confirm Roberts hypothesis. In their view, the phenomenon of 'activated' adsorption cannot be considered as evidence for the heterogeneity of a pure metal surface.

Sommaire : Il est fait référence aux recherches de Beeck *et al.* et Benton *et al.* sur le mécanisme des réactions d'hydrogénation en présence de catalyseurs au nickel. Il est rendu compte d'une expérience faite par l'auteur, qui semblerait confirmer l'hypothèse de Roberts que l'adsorption activée d'hydrogène sur la face du catalyseur est due au fait qu'une partie de cette surface est couverte d'oxygène.

Letter by G. C. A. Schuit & N. H. de Boer *Nature* 168, 15.12.51, 1040-1041

Electron Microscopic Replica Studies of Porosity in Fused Iron Catalysts — 50/I

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The Reaction Between Deuterium and Ammonia on Evaporated Metal Catalysts 51/I

United Kingdom. The preparation of catalysts of high activity and their use in conditions free from the danger of poisoning is a primary essential in fundamental studies of heterogeneous catalysts. Reference is made to research work carried out by Beeck *et al.* who showed how to prepare reproducible surfaces of metal catalysts by the evaporation of pure metal under carefully controlled conditions. Reference is made also to work carried out by Roberts and finally to work carried out by Eley. Examination of simple systems has given much information on the fundamental aspects of catalytic processes but the results of investigations on systems with two reactants are more difficult to interpret. It simplifies matters, if systems of two reactants are investigated by the study of isotopic exchanges since such reactions are almost ideally reversible. The authors chose the ammonia-deuterium reaction for their investigations. The vacuum system used was kept at a pressure of 10^{-6}mm. Hg during operation. The system included a gas purification and storage system, a micro thermal conductivity gauge for analysing hydrogen-deuterium mixtures, the catalyst and the reaction system. The catalyst vessel consisted of a tube 20 mm. diameter 600 mm. long, enclosed in a vapour jacket which could be maintained at any temperature between 410-720°K. Catalysts were deposited by evaporation from a hairpin loop of 0.1 mm. diameter wire. Mercury and tap grease vapours were prevented from entering the vessel by the provision of traps cooled to -45°C during kinetic experiments and -195°C at other times. A small side tube was used for the distillation of ammonia into the vessel before each experiment. For the determination of the rate of exchange the traps were warmed up to -45°C and a measured quantity of ammonia distilled into the small side tube whilst the catalyst was heated to the selected temperature. The deuterium was then admitted, the circulating pump started and an initial reading of the deuterium content taken. At zero time the ammonia was rapidly evaporated in the gas stream by heating the side tube with a large gas flame. The time taken for evaporating the ammonia was less than one second. At suitable intervals samples of gas were removed and analysed. The rate constants were calculated according to a formula given. The fully sintered catalysts prepared from nickel and iron filaments exhibited high stability in the exchange experiments, the activity of these films remaining the same for two to three weeks, as long as the temperatures of the traps was not allowed to rise beyond -45°C. Tungsten films showed an increase in activity with time in all cases. Where the catalyst was maintained at the operating temperature of 710°K the value of the rate constant increased about five-fold at times. No satisfactory explanation could be found for this behaviour of the tungsten films. Experiments on the sintering effects in the case of nickel catalysts showed that rapid sintering decreases the activity of the catalyst but presintering of the films for one hour at the maximum temperature subsequently employed prevented any further change in activity later. Values of the energy of activation are recorded for each metal and some observations on poisoning phenomena are added.

Sommaire : Les caractéristiques catalysantes de films de fer, nickel et tungstène, déposés sous vide, ont été étudiées, en déterminant les constantes du rapport des reactions d'échange ammoniaque-deuterium à différentes pressions et températures.

Article by J. H. Singleton, E. R. Roberts & E. R. S. Winter, *Trans. Faraday Soc.*, **47**, Dec. 1951, 1318-1331

17 — METALLURGY — 17

Vacuum Metallurgy—Its Characteristics and Its Scope 52/I

See Abstract No. : 35/III

Metallography at Elevated Temperatures 53/I

France. The authors built a furnace suitable for the investigation of metal structures at various temperatures. The furnace is fully described. It consists essentially of a base plate which is water-cooled and fits the stage of a Nachet microscope model TM 65. The base plate has a hole in the centre which is sealed by means of a Pyrex window to facilitate observation with the microscope. A disc of refractory material (with a hole in the centre) rests in a recess of the base plate just above the Pyrex window and serves as the specimen support. A cylinder surrounding the specimen support carries the nichrome (heater) winding. The whole assembly is covered with a brass hood which is water-cooled and screwed air-tight to the base plate. A mechanical vacuum pump is provided which facilitates evacuation down to 0.001 mm. Hg. The temperatures required during the experiments rarely exceeded 800°C. A three-way stopcock is inserted in the pipe line connecting the pump with the furnace which controls at the same time a branch line to a storage vessel containing reducing, oxidising or corrosive gases. Whenever the pump was stopped for a short while, a small amount of air leaked into the apparatus and produced colour effects on the surface of the specimen due to oxidation. This colour effect assisted in identifying the orientations of the different grains of the specimen. A similar effect was obtained by admitting hydrogen or a suitable reactive gas through the three-way stopcock. The authors report on research work carried out in this furnace. A specimen of oxygen-free high-conductivity copper was heated to 700°C. Observations through the microscope revealed a structure consisting of twins of three orders of size. A specimen of the same material, polished electrolytically and etched with cold ammonium sulphide, was annealed at 200°C. On admission of air a reddish colour appeared. Renewed annealing of the same specimen at 400°C caused the colour to disappear but it could be seen again as soon as air was admitted. Raising the annealing temperature still further to 600°C, the colour effect vanished but after a short time recrystallisation could be observed. After cooling to about 460°C a dotted appearance became visible in all

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grains and this became even more marked when cooling was continued down to 430°C. At 400°C interference colours were noticed. Since these colour effects could not be attributed to atmospheric oxidation the authors believe that they were due to a crystallisation phenomenon produced by superficial folding of the grains. They termed this effect : ' Tiger Markings '. It is pointed out that the typical pattern of ' Tiger Markings ' has great similarity with surfaces produced by corrosion, whereas ordinary heating *in vacuo* results in a structure similar to that caused by volatilisation.

Sommaire : Description d'une technique et d'un appareil pour l'examen des modifications structurales produites dans des métaux par températures élevées.

Article by J. Maréchal & M. Doucet *Metal Treatment*, **18**, Dec. 1951, 565-571

Applied Vacuum Metallurgy—The Production of Magnesium, Calcium, Tantalum and Zirconium 54/I

See Abstract No. : 41/III

Dollar-a-Pound Titanium 55/I

See Abstract No. : 38/III

Titanium—1951 56/I

United States. The projects and plans of firms which have taken an active interest in the production of titanium are discussed. Various processing methods are mentioned and the essential properties of titanium recorded. The commercial position is reviewed. It is planned to produce 5,000 tons of the metal during 1952 but the whole of this output will be absorbed by government establishments. Private buyers have little chance to be supplied. The present price of titanium is $6 per pound for forgings, bars and rods and $15 per pound for sheets and strips. It is hoped to reduce the price to $1 per pound by improving existing production methods and by raising the volume of production.

Sommaire : Les développements (essentiellement commerciaux) dans le domaine de la production du Titanium sont discutés.

Article by J. A. O'Connor *Chem. Engng.* **58**, Oct. 1951, 136-139

The Hot-Wire Process of Zirconium 57/I

See Abstract No. : 39/III

High Purity Metal 58/I

See Abstract No. : 40/III

Production of Ductile Vanadium by Calcium Reduction of Vanadium Trioxide 59/I

United States. Vanadium is eighth in order of natural abundance of metals useful for structural purposes. In this respect it ranks ahead of nickel and copper but it has only recently been made available commercially in limited quantities. The authors developed a new method of producing ductile vanadium. The method is based on the reaction :—

$$V_2O_3 + 3Ca = 2V + 3CaO$$

The maximum heat reached in this reaction is 1,900°C which is just above the melting point of the metal. The authors used an all Vycor-glass system for their experiments. The first step consisted in reducing V_2O_5 to V_2O_3 in hydrogen at 600°C. The product of this reaction was mixed with calcium and powdered calcium chloride, placed in a container and introduced into a vacuum system. The container had been previously lined with calcium or magnesium oxides. After evacuation to 100 μ Hg argon was admitted to a pressure of 0.8 atm. After the reaction mass had fired, the container was kept at a temperature of 1,000°C for one hour to complete the reduction. The cold charge was then removed from the system and leached with acetic acid. Finally, the vanadium powder was washed several times with water, filtered, and vacuum dried at a temperature of 40-50°C. Some 85% of the original charge (500 grams of V_2O_3) was recovered in the form of vanadium powder. If the vanadium is to be stored in powder form it should be degassed in a vacuum of 0.1-1 μ Hg at a temperature of 400°C to improve its stability. Details of a sintering process are also given and the design of the vacuum furnace used for this process is described. In conclusion, the physical properties of vanadium are discussed.

Sommaire : Une méthode pour la production du vanadium ductile est décrite et quelques propriétés physiques du produit sont données.

Article by E. D. Gregory, W. C. Lilliendahl & D. M. Wroughton *J. Electrochem. Soc.*, **98**, Oct. 1951, 395-399

An Introduction to Arc-Cast Molybdenum and Its Alloys 60/I

United States. Due to its high melting point molybdenum is very attractive as a high temperature structural material. The recently developed process of arc-casting in a vacuum may eventually facilitate larger

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supplies of molybdenum. The size of ingots produced in this process has now risen to 1,000 pounds. The author discusses in great detail the properties of pure molydbenum. In this connection he mentions the hot hardness test, hot hardness being a necessary—if not sufficient—property for good load-carrying capacity of a material at high temperatures. Pure molybdenum shows only limited strength at high temperatures and it is desirable therefore to develop molybdenum-based alloys which overcome this weakness of the pure metal. The author reports on methodic experiments carried out with various molybdenum-based alloys. There are four mechanisms by which the hot hardness of molydbenum can be improved as a result of adding an alloying element: (1) solid solution hardening at equilibrium, (2) solid solution hardening enhanced by supersaturation, (3) augmentation of work hardening and (4) precipitation hardening. Choosing the alloying elements for his experiments the author acted on the assumption that elements which, if added to molybdenum would form hard, brittle and insoluble compounds would not enhance the usefulness of molybdenum. The following transition elements which were soluble in solid molybdenum appeared to be of interest: titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zirconium, columbium, tantalum, and tungsten. As the production process is carried out in a vacuum, the volatility properties of the alloying element are of decisive importance but it has been found that titanium, vanadium, zirconium, columbium, tantalum, and tungsten cause no difficulties on this account. The author also reports on experiments aimed at controlling the hardness of molybdenum-beryllium alloys by a suitable heat treatment.

Article by J. L. Hamm *Trans.A.S.M.E.* **73**, Aug. 1951, 723-732 see also *Engineer*, **102**, 28.12.51, 830-831

Sommaire: Les propriétés du molybdène fondu à l'arc sont étudiées et des recherches faites en vue d'obtenir un alliage convenable, augmentant la dureté du métal pur.

Molybdenum A New High Temperature Metal

61/I

United States. Recent developments in jet engines, gas turbines, rockets, etc., have given fresh impetus to the development of heat-resistant materials. Molybdenum's high melting point (4,760°F), its abundance and availability make it a material unique for use as a refractory. It is estimated that nearly a million pounds a week could be absorbed by industry. The United States has so far produced 90% of the world's supply. The most important single source of supply is the deposit of molybdenite at Climax, Colorado. Details are given of the process, by which molybdenum is manufactured at Climax. The material is melted in an arc *in vacuo* which operates between a vertical consumable molybdenum electrode and a bath of the liquid metal. The provision of a special die, through which the molybdenum powder is fed into the furnace, avoids the risk of contamination. As a by-effect of the process the molybdenum is purified to a certain degree during the melting and its oxygen content lowered to 0.003% or less. Methods for forming and shaping molybdenum by rolling, machining, stamping and spinning as well as methods for joining by brazing and welding have already been worked out. However, the properties of the pure metal are not fully explored yet. This applies, in particular to the factors which control its ductility. Pure molybdenum is lacking in surface stability. Above 1,400°F MoO_3 is formed and vaporises at an appreciable rate, even if the atmosphere contains only a few per cent. of oxygen. To counteract this, cladding with nickel or inconel has been suggested, also the deposition of silicon and ceramic coats and electro-plating, but it appears that the only really effective means would be the alloying of molybdenum with an element which suppresses the formation of volatile MoO_3. For this reason investigations into molybdenum alloying rank among the most important research projects now under way.

Article by R. M. Parke *Metal Prog.*, **60**, July 1951, 81-96

Sommaire: Revue des developpements dans la fabrication du molybdene et de ses alliages, suive d'une discussion des propriétés physiques du molybdene.

II — Vacuum Apparatus and Auxiliaries — II

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20 — PUMPS — 20

Modern Vacuum Pumps 1/II

United Kingdom. There are two distinct classes of vacuum pumps, the mechanical and the vapour pump. The normal mechanical or rotary pump produces a vacuum of 5-10 μ Hg. The performance of these pumps depends largely on the accuracy of machining, the vapour pressures of the oil used, and finally, on the degree of contamination of the oil with condensable vapours. There are rotary pumps which eliminate the condensable vapours, for example the gas ballast pump, in which air is bled into the pump on the exhaust side during the compression cycle, so that the expelled gas vapour mixture does not become saturated. Rotary pumps are made in a wide range of sizes of volumetric displacement from a fraction of 1 ft.^{3}/min. up to about 700 ft.^{3}/min. To increase their capacity two- or more stage pumps are built. Series-parallel arrangements are also used. Molecular pumps are mentioned but the precision required in their construction has so far discouraged their application except for laboratory purposes. A detailed description of the Langmuir and Gaede design of diffusion pumps is given. The principle of the operation of diffusion pumps is explained. Their performance is governed by the vapour pressure of the pump fluid which determines the ultimate pressures obtained, the Ho coefficient which is defined as the ratio of the observed pump speed measured as the volume of gas pumped per unit time at a given pressure to the theoretical speed of diffusion through an orifice of the same area as the pump slit (11.7 l./sec./cm^2 for air). Mercury would be the ideal pumping fluid but for its comparatively high vapour pressure at room temperature (10^{-3}mm. Hg). Vacuum distilled mineral oils, more recently introduced as pump fluids, have vapour pressures around 10^{-6} to 10^{-7}mm. Hg. Certain synthetic oils are also employed. The danger of decomposition can be minimised by the use of the fractionating or purifying type of pump. Silicon oils are claimed to have better resistance to oxidation than other oils. The capacity of the backing pump should be greater than that of the diffusion pump for the critical range at which the capacity of the vapour pump starts to fall off, *i.e.*, the capacity of the pumping unit as measured at the diffusion pump slit must increase with increased pressure throughout the whole range from atmospheric downwards, otherwise it is difficult to achieve short evacuation times and to deal with gas bursts and pressure surges. In conclusion, the author calls for more research work to give a better understanding of the working mechanism of the diffusion pump.

Sommaire: La situation actuelle concernant la construction et les applications de pumpes rotatives et à diffusion est présentée. Des détails sur les fluides de pompage et leurs développements sont ajoutés.

Article by D. R. Goddard *J. Sci. Instrum.* Suppl. 1, 1951 1-7

Automatic Lubricator for a Rotary Vacuum Pump 2/II

See Abstract No. : 32/II

Refrigeration of Oil Diffusion Pump Baffles 3/II

See Abstract No. : 33/II

Investigations into the Ultimate Pressures of Diffusion Pumps Designed to Purify their Working Fluids 4/II

United Kingdom. A diffusion pump which powerfully purifies its fluid from contaminants and decomposition products can produce very low pressures as quickly with a fluid of commercial quality as it can with a specially prepared fluid. This is demonstrated by comparative tests on pumps designed to purify continuously their working fluids with varying efficiency, and operated with proprietary pumping fluids and with commercial plasticisers. Fluid decomposition may contribute both permanent gas and vapour components to the ultimate pressure so that in certain cases only a moderate improvement in ' ultimate ' can be obtained by the use of a refrigerated trap. In a pump designed to keep the concentration of decomposition products in its fluid at a very low level, the rate of evolution of gaseous products is reduced, probably because intermediate products of fluid breakdown tend to be removed before they finally decompose into gases. In addition to the much lower total pressure which may be obtained by such a pump, the applications of a refrigerated trap may be much more effective. These advantages can be obtained in a pump of rugged and simple design without prejudice to other performance characteristics.

Sommaire : Travaux de recherche portant sur les pompes de diffusion à extrême pression pour la purification de leurs fluides.

Article by D. Latham B. D. Power & N. T. M. Dennis *Vacuum*, 1, April 1951 97-114

An Assessment of Some Working Fluids for Diffusion Pumps 5/II

United Kingdom. Since oils were first suggested as alternatives to mercury as pumping fluids for diffusion pumps, a very large number of organic and semi-organic materials have been applied to this use. All these have differing characteristics which may affect the choice of fluid for a particular application, while the use of mercury itself is still essential in some cases and desirable or at least defensible in others. The authors discuss how some of the characteristics of a selection of pumping fluids would influence a user in his choice, and illustrate the discussion with some of their own experiences and experiments.

Sommaire : Les auteurs de l'article tâchent d'établir une juste estimation de certains fluides actifs pour les pompes de diffusion; prenent en particulière considération diverses huiles de nature organique ou semi-organique.

Article by D. Latham B. D. Power & N. T. M. Dennis *Vacuum*, 2, Jan. 1952 33-49

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Determination of the Molecular Weights of Low Vapour Pressure Oils and Greases 6/II
See Abstract No. : 39/I

21 — GAUGES — 21

On the Conduction of Heat in Rarefied Gases and Its Manometric Application. I. 7/II

Holland. Formulae for the conduction of heat in pure gases and in binary mixtures relevant to a tube with a thin, axial heated wire are developed. They cover the region of pressure between that for which the heat conduction is independent of pressure and that for which Knudsen's formula is valid. A theory for precision manometry is given and the manometric constants for twenty-five gases have been measured.

(*Science Abstracts*)

Sommaire: Formules pour amener la chaleur dans les gaz purs et dans les mélanges de gaz binaires; on en exposé les applications à un tube muni d'un mince fil-de-fer chauffé axialement.

Article by H. von Ubisch *Appl. Sci. Res.*, **A2**, (No. 5-6) 1951 364-402

On the Conduction of Heat in Rarefied Gases and Its Manometric Application. II. 8/II

Holland. The geometrical design of tubes for manometers, the design of circuits and the properties of direct-reading hot-wire manometers are investigated. Examples of improved manometers are given. Further possible improvements and leak-hunting are discussed.

(*Science Abstracts*)

Sommaire : Etude des properiétés des manomètres à fils chauds et à lecture directe.

Article by H. von Ubisch *Appl. Sci. Res.*, **A2**, (No. 5-6) 1951 403-430

Review of Vacuum Gauges 9/II

United Kingdom. A short account is given of methods for measuring pressures below 10 mm. Hg. The McLeod gauge, thermal conductivity gauges, viscosity, ionisation and Knudsen gauges are discussed in detail and their limitations for accurate measurements are pointed out. The industrial application of gauges and their use as protective devices is also discussed. 50 references.

(*Author*)

Sommaire: Bref rapport sur les méthodes de mesure au dessous de 10 mm. Hg, et les limites de chacun des différents principes de mesure.

Article by W. Steckelmacher *J. Sci. Instrum.* Suppl. 1, 1951. 10-19

Techniques and Equipment for Measurement of Very Small Gas Pressures. I. Vacuum Gauges without Amplifier and Methods of Measurement for Vacuum Gauges with Amplifier 10/II

Germany. Brief descriptions of the different types of vacuum gauges include on one hand those without amplifier, namely, mechanical or feather elastic and U-tube manometer, and those needing amplifiers, namely compression, heat-conducting, friction, radiometric, and ionisation vacuum gauges.

(*Nuclear Science Abstracts*)

Sommaire : Article passant en revue les divers types de jauges sous vide, avec et sans réglage d'amplificateur

Article by H. Schwarz *Arch. Tech. Messen.* **188**, Sept. 1951 T96-T97

New Trends in Vacuum Research Based on Ionisation Phenomena 11/II
See Abstract No. : 2/I

Notes on the Ionisation Gauge 12/II

United Kingdom. Eight gauges are required to record the true average pressure in the vacuum chamber of the synchrotron at the University of Birmingham. It is important that these gauges give accurate measurements in the region of 10^{-6}mm. Hg. or below. The hot filament type of ionisation gauge has been found to be the most suitable for the purpose. All details of the gauges used are given. Generally speaking, they are of the well known triode type enclosed in a hard glass envelope and fitted with filaments of thoriated tungsten. The sensitivity of the gauges is defined as $S = I/ip$; where I is the ion current, i is the electron current and p the pressure in mm. Hg (below 10^{-4}mm. Hg). The gauges used behave linearly but their sensitivity is reduced in the pressure range of 10^{-4} to 10^{-3} mm.Hg. Experimental and calculated values for the sensitivity of the type of gauges employed in the synchrotron are given for various atmospheres in Table I which is reproduced below in abbreviated form :—

Absolute Sensitivity of Gauges

Gas	*Dry Air*	*Nitrogen*	*Oxygen*	*Hydrogen*	*Argon*
$S_{expt.}$	17.0	21.0	24.0	8.0	22.4
$S_{calc.}$		17.2			21.0

(all values quoted apply to pressures below 10^{-4}mm. Hg)

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The pumping action of these gauges for oxygen has been investigated. The expected rate of oxygen adsorption has been calculated to be 0.26 litres/second. This is roughly confirmed by experiment. The pumping of vapours and gases originating from the diffusion pump is based on a somewhat different mechanism from that assumed for the cold-cathode ionisation gauge. It has been stated previously that no pumping effect could be observed when the glass envelope of the gauge was operated at a temperature above 200°C, whilst the collector was running at a temperature of 280°C. It can be assumed therefore that the glass envelope is the actual sorbing surface, *i.e.*, the oil decomposition products dissociate upon collision with the hot filament and are sorbed by the surrounding cooler surfaces. The influence of the gauge tubulation on the pressure reading of the instrument is demonstrated in a table.

Sommaire : La sensibilité de la jauge à ionisation à cathode chaude a été etudiée et les différents aspects de son effet de pompage aux très basses pressions examinés.

Article by L. Riddiford *J. Sci. Instrum.* **28**, Dec. 1951 375-379

On the Application of a Philips Ionisation Gauge Type of Ion Source in a Mass Spectrometer Leak Detector 13/II

See Abstract No. : 41/II

Electronic Manometer Measures Minute Pressures 14/II

United States. The micromanometer referred to was constructed for use with a mass spectrometer and gives direct readings of pressure on a scale that can be calibrated in units of pressure.

(*B.S.I.R.A. Bulletin*)

Sommaire : Description d'un micromanomètre destinè à être employé avec le spectromètre de masse.

Note by Anon. *Mach. Design* **23**, Aug. 1951 119

Knudsen Gauges 15/II

United Kingdom. A brief review of the development and applications of the Knudsen gauge is followed by a detailed description of improved forms of metal and glass gauges. Their performance with respect to factors such as outgassing, methods of suspension, extension of range by electro-magnetic compensation, and damping are discussed. The theory of the absolute manometer is reviewed. In particular, the fundamental assumptions concerning accommodation coefficient, the edge effect due to large heater-to-vane distance, and vane temperature in the low pressure (Knudsen) region are discussed. A theory is developed to give a correction factor for a rectangular vane and heater valid for any dimensions and distance. It is shown that under certain conditions calibration is independent of the temperature of the vane.

Sommaire : Bref compte rendu sur le développement et les applications de la jauge de Knudsen, suivi de la description détaillée de formes améliorées de jauges métalliques et en verre.

Article by W. Steckelmacher *Vacuum* **1**, Oct. 1951 266-282

A New All-Glass Membrane Manometer 16/II

United Kingdom. In pressure measurements involving substances which might attack mercury all-glass manometers are particularly useful. The authors refer in particular to manometers of the diaphragm type, where the corrosive gas, the pressure of which is to be measured, is kept on one side of the diaphragm and a mercury manometer is connected to the system on the other side of the diaphragm. Details are given of a new design developed by the authors. The diaphragm of the new manometer is in contact with a vertical lever, which consists of a glass tube and contains a platinum wire, suspended from a glass spring. The zero position is checked by electrical contact with the platinum wire. The diaphragm has a diameter of about 2 cm. and is kept as thin as possible. This gauge has been used with success for the measurement of the vapour pressures of stannic halides in the temperature range 20-340°C. The gauge facilitates readings with a precision of 0.1 mm. Hg. The variation of the zero setting is less irregular than is the case with other gauges of this type. It should be useful in all instances, where the measuring procedure requires successive heating and cooling of the gauge.

Sommaire : On donne les détails d'un manomètre à membrane entièrement en verre employé avec succès pour le mesurage de la pression de vapeur des halogènures stanniques en températures variant de la température atmosphérique jusqu' à environ 340°C.

Note by A. Kabesh & R. S. Nyholm *J. Chem. Soc.* Nov. 1951 3252-3253

A Sensitive Differential Manometer 17/II

Canada. A description is given of a differential manometer of small volume, developed by the author for a special purpose. It is capable of a precision of 0.1 to 0.2 micron Hg. The instrument consists of two measuring cells each connected to nearly identical oscillator circuits and is of the diaphragm gauge type, where the diaphragm is one plate of an electrical condenser. In this case the mercury surface serves as the diaphragm. For most measurements the distance between condenser plate and mercury surface in each of the two cells was held at 1.3 mm. Both measuring cells were mounted on a brass plate which in turn was bolted to a concrete base, resting on shock absorbers. Vibration was not eliminated altogether, but reduced to an amount which did not interfere with the measurements. Changes in temperature had some effect on the position of the mercury levels and had to be taken into account when operating the instrument. A wire sealed into the bottom of the manometer connected the total mass of mercury to the ground and thus acted as a return lead

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to the oscillators. A change of pressure changed the capacity in the two oscillator circuits in opposite directions. The beat frequency of the oscillator was compared on an oscilloscope with the output of an audio-signal generator with a very high frequency stability in the range of 1,000 to 100,000 cycles/second. Details are given of the electrical circuit. A mathematical analysis of the operation of the instrument is added. The manometer may be used for highly accurate measurements over a small pressure range or for less accurate measurements over a wide pressure range.

Sommaire : Description d'un manomètre différentiel au mercure de construction spéciale.

Article by J. M. Los & J. A. Morrison *Rev. Sci. Instrum.* **22**, Nov. 1951 805-809

Determination of Mercury Level in a Steel-Tube Manometer

18/II

United Kingdom. A device for reading the mercury level in a steel-tube manometer is described which consists of a radiation source emitting a beam of gamma rays which penetrates the steel-tube of the manometer and enters into an ionisation chamber detector on the opposite side. The ionisation current passes through a resistance connected to the grid circuit of the electrometer valve, the output of which is amplified and fed to the Y_1-plate of a cathode ray tube. The potential of this plate is thus proportional to the intensity of the radiation reaching the chamber. When the radiation passes through the mercury column the ionisation current is low, but if the mercury has not reached the level of the radiation path the ionisation current is high. Intermediate values occur, where the narrow beam passes through the meniscus of the mercury, the exact value being determined by the proportion of mercury and air included in the beam. The radium source is mounted in a lead pot giving protection in all directions except on a line through the manometer tube. The latter is screened by the ionisation chamber itself. Details of the design are discussed and an electrical circuit diagram is shown.

Sommaire: Description d'un dispositif par lequel la hauteur de la colonne de mercure dans un tube en acier peut être déterminée. Il consiste en une source radiactive comme émitteur et une chambre à ionisation comme récepteur.

Article by R. Meakin *J. Sci. Instrum.* **28**, Dec. 1951 372-373

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22 — MEASURING PLANT (VACUUM) — 22

Application of the Mass Spectrometer to High Vacuum Problems

19/II

United Kingdom. Details are given of an investigation into the composition and behaviour of residual gases in ordinary dynamic vacuum systems. Two different types of mass spectrometers were used for the experiments. One of the tubes was constructed throughout from silica glass and copper and was entirely free from demountable joints, the other was made of brass or stainless steel and was fitted with rubber gaskets. The former type was evacuated by mercury diffusion pumps, the latter by oil diffusion pumps. Examining the conditions during the initial evacuation period it was found that the oxygen pressure was less than 10^{-7}mm. Hg after 20 minutes of pumping and less than 10^{-8}mm. Hg after one hour of pumping. 70% of the ions present were formed from water and most of the remainder from hydrocarbon vapours. The carbon monoxide concentration was about 3% of that of the water. The conclusion is that in the early stages of an evacuation process the concentrations of all kinds of molecules diminish at approximately the same rate. In another series of experiments the effects of low temperature baking have been investigated. After stabilising the residual pressure the system was baked at 100°C for a period of 4 hours and the temperature of the cold trap maintained at −78°C. This experiment proved that water cannot effectively be removed in these conditions. It is merely transferred to the cold surface from which it re-evaporates, a typical case of a ' virtual leak '. Analysing the residual gases prevailing at extremely low pressures it was found that constructional methods and pump fluids had very little influence on the composition of the gases unless high temperature baking was employed. In all trapped systems the more abundant residual was water. The residual hydrocarbon pressure was higher in systems served by oil diffusion pumps than in those served by mercury pumps but the difference was not very marked. The presence of hydrocarbon molecules in systems evacuated by mercury diffusion pumps even if properly baked and trapped can be explained as follows : In the intitial stage of evacuation, the diffusion pump cannot be switched on for fear of oxidation and the cold trap cannot be cooled because this would cause condensation of large quantities of water. At this stage oil molecules from the rotary pump diffuse throughout the system and some of them are absorbed on the fine side. Even prolonged high temperature baking and the application of cold traps at the temperature of liquid nitrogen seldom succeeds in removing these molecules completely. It appears advisable, therefore, to place an active carbon trap between the rotary and diffusion pump if very low pressures are to be obtained.

Sommaire : Le spectromètre de masse a été utilisé pour l'étude de la nature et le comportement de gaz résiduels dans un système normal dynamique à vide.

Article by J. Blears *J. Sci. Instrum.* Suppl. 1, 1951 36-42

A Cold-Cathode Mass Spectrometer Leak Detector

20/II

See Abstract No. : 40/II

II — Vacuum Apparatus and Auxiliaries — II
Contd.

Abstract No. and References

On the Application of a Philips Ionisation Gauge Type of Ion Source in a Mass Spectrometer Leak Detector — 21/II

See Abstract No. : 41/II

Leak Detection with a Mass Spectrometer Using Hydrogen Gas — 22/II

See Abstract No. : 42/II

Process Control by Mass Spectrometer — 23/II

See Abstract No. : 46/I

The Electron Microscope and Its Industrial Application — 24/II

United Kingdom. The unaided eye cannot separately distinguish two points lying less than 0.1 mm. apart. The light microscope has a resolution limit of approximately 0.5 λ. The theoretical resolution limit of the electron microscope is 0.03Å, the practical limit is approximately 40Å. The operation of an electron microscope is based on the fact that electrons can be deflected by either electrical or magnetic fields, both principles being used in the form of electron lenses. An electron microscope essentially consists of an electron gun producing electrons which are artificially accelerated to the required energy and travel through the chamber in a diverging beam. By means of an electron condenser lens this diverging beam is converted into a parallel beam directing the electrons to the specimen. Below the specimen is an objective lens magnifying the image from 50x to 100x. Finally, a projector lens is provided, giving an additional magnification of 175x. Thus the total magnification produced by the instrument is 17,500x. The provision of a second projector lens may increase this figure to 100,000x. The tube is evacuated to 10^{-5}mm. Hg during operation. To allow for the manipulation of the photographic plate and the specimen without breaking the vacuum in the tube air locks are fitted to the instrument in a suitable position. Special techniques have been developed for the preparation of specimens to be used in the electron microscope. The specimen must be mounted on a support which does not stop the transmission of electrons, *i.e.*, the mounting films should not be thicker than 200 Å. The specimen itself has to withstand high vacuum conditions and must be dry. Various specimen preparation techniques are discussed, including shadow-casting. Finally, replica techniques are mentioned. In conclusion the author calls for the development of new specimen preparation techniques which facilitate effective examination of living organisms in the electron microscope.

Sommaire : Discussion de la théorie, de la construction et des applications du microscope électronique.

Article by J. W. Sharpe *Chem. & Industr.* 17.11.51. 976-981

Carbon Gel as Revealed by the Electron Microscope — 25/II

See Abstract No. : 30/II

Electron Microscopic Replica Studies of Porosity in Fused Iron Catalysts — 26/II

United States. A typical fused iron (Fe_3O_4-MgO-K_2O) synthetic ammonia catalyst was to be examined under the electron microscope after reduction in hydrogen. The raw catalyst consisted of a solid solution of magnetite and the structural promoters. Prior to the reduction there was virtually no porosity or internal surface area. As a result of the volume change in the transformation from magnetite to alpha-iron during the reduction in hydrogen, a fine porous structure with a high surface area was formed. The average dimensions of these pores were estimated at 370 and 800 Å for reduction temperatures of 450°C and 550°C respectively. The examination of replicas taken from the surface of the reduced catalyst in the electron microscope roughly confirmed these estimated pore sizes. Details are given of two methods employed for the production of the replicas, negative formvar and positive silica replicas. Pieces of the catalyst were polished on one surface prior to reduction and after reduction dipped in a 0.5% solution of formvar in ethylene dichloride. Subsequently, a 10% solution of nitro-cellulose in butyl acetate was spread over the surface, dried and the double film peeled off. The replica was shadowed with chromium evaporated at an angle of 10° with the film surface. Finally, the specimen screen was fastened to the formvar side of the film and the assembly dipped in amyl acetate, in order to dissolve the nitro-cellulose. After drying the specimen was ready for use. In the case of the silica replica, a 10% solution of nitro-cellulose was spread on the metal surface, dried and the film peeled off. Subsequently silica was evaporated on to the replica and in some instances the replica was shadowed in addition with chromium. The nitro-cellulose was dissolved in the manner described before.

Sommaire : On donne des détails sur les reproductions de techniques pour l'étude de la porosité dans des catalyseurs en fer fondu sous le microscope électronique.

Article by L. T. McCartney & R. B. Anderson *J. Appl. Phys.* **22**, Dec. 1951 1441-1443

Production of Small Apertures by Evaporation Techniques — 27/II

See Abstract No. : 64/III

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II — Vacuum Apparatus and Auxiliaries — II
Contd.

Abstract No. and References

26 — MATERIALS — 26

Continuous Mercury Still — 28/II

United States. The author describes a mercury still which represents a development of the design proposed by Helinek, Huber and Astle, eliminating all complicated glass work. After the removal of all particulate matter, the mercury to be distilled is poured into a reservoir. A vertical glass tube, 74 cm. long and 6 mm. diameter, connects the reservoir with the distillation chamber which is heated by gas. After having passed through the distillation chamber the clean mercury drops through another vertical glass tube, 76 cm. long and 2 mm. wide, into a receptacle. A rotary pump protected by a trap is connected to the delivery tube. To start operation, the vacuum pump is switched on and the heat applied. In order to make sure that all air and moisture is removed from the system, distillation with the pump operating is continued for about 1 hour. Subsequently, the rotary pump is switched off and disconnected and the distilled mercury allowed to collect in the delivery tube to a height of 76 cm. The still is now ready for continuous operation. At this stage the introduction of mercury into the still and the collection of the clean mercury at the other end are accomplished under atmospheric pressure, whereas the actual distillation takes place in a completely sealed and evacuated space. The still supplies clean dry mercury at the rate of 600 grams per hour.

Note by P. B. Hamilton *Analyt. Chem.* 23, Oct. 1951 1526

Sommaire : Description d'un alambic pour le nettoyage du mercure par distillation, capable d'un rendement de 600 grammes à l'heure.

Uses of Activated Alumina — 29/II

United Kingdom. Aluminium oxide is known as alumina, hydrated aluminium oxide as activated alumina. The oxide itself, Al_2O_3 can be derived from the mineral corundum. The mono-hydrate $Al_2O_3.H_2O$ is derived from diaspore and bauxite; $Al_2O_3.3H_2O$ is obtained from hydrargillite or gibbsite. Activated alumina is available as a porous, granular and chemically inert solid and has a high capacity for the adsorption of moisture. It retains moisture by physical adsorption as distinct from other drying agents which either react chemically with the water or absorb it. Activated alumina is successfully used for the drying of gases. Its efficiency in this application depends on the rate of flow of the gas and the temperature. In the case of normal rates of flow it may absorb from 16-18% of its weight of water to give a commercially dry gas having a water content of about 0.04 grains/cubic ft. Details are given of the various applications of activated alumina in industry. It is applied to the drying of transformer oil, refrigerants and in certain cases to the drying of solids. Finally, reference is made to its use as a catalyst.

Article by Anon. *The Times (Industr. Suppl.)* Dec. 1951 27

Sommaire : Description de l'origine, des propriétés et de la performance de l'oxyde d'aluminium activé, qui est un important agent de séchage.

Carbon Gel as Revealed by the Electron Microscope — 30/II

United States. The electron microscope has been instrumental in giving proof of the existence of reticulate chain structure in carbon black and the degree, to which this structure persists through various stages of processing a carbon reinforced rubber compound. It was shown that these persistent chains are the primary factor in the development of hardness properties. Another concept which may affect the development of modulus resilience and actual road wear of cold rubber treads, is the carbon gel complex, first mentioned by Sweitzer et al. The investigation reported here was initiated to substantiate Sweitzer's claims. It deals with low temperature polymer gels only. Baker had previously published electron micrographs of microgels, which were concerned with gelation within latex particles and which showed contoured microgel structures against a structureless sol background. This differentiation between sol and gel introduced by Baker originally has been maintained. As the present work deals with large units of macrogel, found after coagulation and intimately associated with carbon black, new preparation techniques had to be developed, details of which are given in the article. The cold rubber gel was formed by heating the raw polymer in an oven of 400°F for one hour. The gel and sol portions of the polymer were separated using benzene in a Soxhlet extractor. The gel was then spread on formvar film and shadow-cast with chromium. The sol specimen was prepared by drying the sol and the swelling action of benzene on the gel was simulated by swelling the sol in a mixture of benzene and alcohol. A piece of the solution mass was then spread on the formvar film. The micrograph of the sol showed a diffused type of material, whereas the appearance of the gel shows as a shredded type of material. In conclusion the authors state that high temperature mixing produces a carbon gel which is highly pigmented and at the same time a polymer gel, free of carbon; the sol rubber remaining shows a very low concentration of free carbon. It is suggested that the combination of highly pigmented units separated by 'soft' unpigmented areas and areas of low carbon concentration gives the high modulus properties previously associated chiefly with highly loaded stocks.

Article by W. A. Ladd & M. W. Ladd *Industr. Engng. Chem.* 43, Nov. 1951 2564-2568

Sommaire : On a procédé à des études pour vérifier la conception du complex de congélation au carbone suggérée par Sweitzer, comme élément essentiel d'amélioration des risques d'usure routière caracteristique des surfaces de roulement du caoutchouc.

A High Temperature Vacuum Induction Furnace — 31/II

See Abstract No. : 46/III

II — Vacuum Apparatus and Auxiliaries — II
Contd.

Abstract No. and References

28 — APPARATUS COMPONENTS — 28

Automatic Lubricator for a Rotary Vacuum Pump — 32/II

United Kingdom. A lubricator is described and shown in a sketch, which facilitates the supply of oil to the rotary blades of a vacuum pump at a uniform rate. The action of the apparatus is fully automatic and confined to the periods when the pump is working. It essentially consists of an oil reservoir connected to the pump housing on the suction side by means of a vertical feeding tube. The flow of oil is originated by the suction produced in the pump. The feeding rate can be controlled by a needle valve. The oil dripping off the end of the feeding tube is carried into the pump by the air stream.

Sommaire : Un graisseur automatique pour des pompes à palettes est décrit.

Note by Anon. *Machinery* 15.11.51. 869

Refrigeration of Oil Diffusion Pump Baffles — 33/II

United Kingdom. A study has been made of the effect of reducing the temperature of the baffles fitted to diffusion pumps on the oil vapour pressure in the evacuated system. During the experiment the baffles, normally cooled with water, were cooled with alcohol. Thus a temperature of –60°C was achieved. Details are given of the experimental arrangement.

Sommaire : Etudes de l'effet de la réduction de la température du piége (baffle) d'une pompe à diffusion sur la réduction de la pression de vapeur de l'huile dans un système évacué.

Letter by R. S. Barton & A. H. Turnbull *Vacuum* 1, April 1951 117-118

Leaks in Vacuum Liquid-Air Traps — 34/II

United Kingdom. A number of liquid-air traps have been built which were to be suspended in pumping manifolds at the heads of 16 inch diffusion pumps. The traps were made of stainless steel consisting of a cylindrical centre piece, 5 inches long, and two-spherical end caps. All joints were welded. The traps were tested at room temperature and any leaks found were corrected by hard-soldering with ' Easy-Flo ', to give a leak rate of the order of 0.01 µl per second. In order to arrange for a test under working conditions the traps were then placed in a flask containing liquid air. It was found that a great number of leaks previously treated were still giving trouble and the attempt to correct the leaks by soldering proved unprofitable. The best solution seemed to be re-welding instead of hard-soldering. It was also found that leaks not previously treated showed leakage rates about 10 times as high in the presence of liquid air than under room temperature conditions. It was established that this increase was due to a penetration of the liquid-air into the holes and not to severe stresses imposed as a result of refrigeration. It appears that the leakage rates permissible for liquid-air traps should be some 100 times lower than those for the rest of the equipment.

Sommaire : Des pièges à air liquide soudés en acier inoxydable ont été examinés en vue des fuites et il à été trouvé recommendable, de réduire le degré de fuite admissible par un facteur de cent, par rapport au reste de l'installation, lorsqu'on utilise de l'air liquide comme réfrigérent.

Letter by L. Riddiford & R. F. Coe *J. Sci. Instrum.* 28, Nov. 1951 352-253

Greaseless Stopcock for Use at Sub-Atmospheric Pressures — 35/II

United States. Operating an Othmer equilibrium still, it was found that a liquid sampling stopcock lubricated with silicone grease gave trouble. Small amounts of the grease dissolved out of the stopcock and mixed with the still contents, rendering all determinations unreliable. To overcome this difficulty, a leakproof stopcock was designed similar to the type suggested previously by Newman. A standard taper male joint was sealed to the stopcock and a receptacle of 50 ml. volume attached. The latter was connected with a side arm to the vacuum manifold. As a result the pressure drop across the stopcock was reduced to the amount caused by the small hydrostatic head of the liquid contained in the apparatus. Thus, the danger of contaminating the still contents was eliminated if a leak developed; the liquid and any lubricating medium used in the stopcock would collect in the small receiver.

Sommaire : Description de la construction d'un robinet d'arrêt pour emploi avec alambics sous vide et qui évite la contamination du contenu de l'alambic par le matériaux utilisé pour le graissage du robinet d'arrêt.

Note by K. C. Buchman *Analyt. Chem.* 23, Nov. 1951 1724

Compressed Air Operated Valve for Use in Straight Pipe Lines of Vacuum Evaporation Plant — 36/II

France. The valve described is of the diaphragm type and operated by compressed air. The diaphragm is made of rubber sheeting 2-3 mm. thick. In the open position of the valve the gas flow through the pipe is unobstructed. A sketch is given showing the valve fitted to a pipe line of 60 mm. diameter.

Sommaire : L'on décrit une vanne à membrane laquelle à l'état ouvert ne cause aucune obstruction à l'écoulement du gaz par le tuyeau.

Note by P. Prugne *J. Phys. Radium* 12, Oct. 1951 66A

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Abstract No. and References

Experiments with Metal Foil as a High Vacuum Packing Material

37/II

Germany. Details are given of the performance of aluminium foil as a packing material for vacuum-tight flanged pipe joints. The design of the flanges and the processing of the foil necessary to give satisfactory results is discussed. The joints can be exposed to ordinary baking temperatures up to 280°C.

Sommaire : Rapport sur la construction et les propriétés de raccords du type à flasque, utilisant comme joints, des feuilles d'aluminium.

Article by H. Hinterberger *Z. Naturforsch.* **6a**, Aug. 1951 459-462

29 — MISCELLANEOUS APPARATUS — 29

Photo-Electric Vacuum Controller

38/II

United States. Many existing pressure control devices are of little use, if applied in precision vacuum distillation processes, as they require intricate glass work, involve the use of metal-to-mercury contacts which are liable to become dirty and need a separate pressure gauge for setting and checking the controller. A new device is described which permits direct setting of the instrument at the desired pressure, continuous reading of the pressure during operation and the elimination of metal-to-mercury contacts. It has been specially developed for application in connection with the distillation of fatty acid esters. It consists essentially of a lamp, suitably shielded, which emits a light beam though a 1 mm. pin hole in the shield. The light beam is directed to a photocell, which in turn is connected to a relay. The latter remains closed as long as the light beam energises the photocell but if the pressure in the system rises, the float of a Dubrovin gauge penetrates into the space between the photocell and the lamp and interrupts the light beam. As a result, the relay opens. In this manner the operation of vacuum pumps can be controlled continuously during a run.

Sommaire : Description d'un dispositif de règlage de la pression, utilisant une jauge de Dubrovin comme élément règleur.

Note by C. G. Youngs T. M. Mallard & B. M. Craig *Canad. J Technol.* **29**, Oct. 1951 447-450

A Simple Method of Leak Detection in High Vacuum Apparatus

39/I

Germany. A 10^{-5}M to 10^{-4}M alcoholic solution of fluorescein or eosin is painted on the suspected areas of the vacuum apparatus, which is then evacuated to at least several mm. Hg. After 2 or 3 minutes the excess fluorescent solution is removed, and the glass is irradiated with ultraviolet light. All holes and surface defects are thus located. A high-frequency electrode may then be used to distinguish leaks from other defects.
(*Nuclear Science Abstracts*)

Sommaire : Description d'une méthode simple pour la détection de fuites en appareil sous vide, en faisant emploi d'une solution fluorescent irradiée avec rayons lumineux ultraviolets.

Note by E. Volcker *Z. Naturforsch*, **6a**, Sept 1951 512-513

A Cold-Cathode Mass Spectrometer Leak Detector

40/II

United Kingdom. A full description is given of a mass spectrometer leak detector, fitted with a cold-cathode ion source, instead of a hot-cathode employed in the conventional design. The cold-cathode ion source has a much longer service life (several hundred hours) than the hot filament which is reported to last only a few hours, in mass spectrometer leak detectors at least. Details of the electrode arrangement, the electrical circuit, and the vacuum system are discussed and illustrated in sketches. The instrument is of the 180° type with 4.5 cm. radius. A typical mass spectrum obtained by varying the magnetic field at constant accelerating voltage is shown. The provision of an a.c. amplifier for the ion current in conjunction with velocity modulation of the ion beam, greatly reduces background effects. Where difficulties with background were due to the presence of residual organic vapours, these have been largely overcome by the use of silicone oil instead of Apiezon oil in the diffusion pump. The instrument was applied to the examination of a specific type of u.h.f. valves which were found to turn soft a few days after sealing. In the course of this investigation, leaks as small as 10^{-5} μl/sec. have been detected with this instrument.

Sommaire : Description de la composition et discussion de la performance d'un spectromètre de mass qui utilise une source d'ions à cathode froide, pour la détection de fuites.

Article by C. J. Milner *J. Sci. Instrum.* Suppl. 1, 1951 29-36

On the Application of a Philips Ionisation Gauge Type of Ion Source in a Mass Spectrometer Leak Detector

41/II

Holland. The development of mass spectrometers designed for use as leak detectors is reviewed. The use of the Philips ionisation-gauge type of ion source is suggested instead of hot filaments. The focusing arrangement in the instrument mentioned consists of an homogeneous electrical field perpendicularly superimposed on to a homogeneous magnet field. As a result, the ions travel on a cycloid path independently of the initial velocity and angle, at which they may enter the fields. The proposed arrangement has 3 advantages : (1) a high-intensity ion current, (2) a sharp focus and (3) the elimination of the need for replacing filaments.

Sommaire : Discussion du développement de la construction des spectromètres de masse utilisés comme detecteurs de fuites. L'attension est attirée sur l'avantage que présente l'emploi d'une source d'ions du type jauge Philips dans cet instrument.

Article by N. N. Warmoltz *Appl. Sci. Res.* **B2**. No. 1. 1951 61-65

II — Vacuum Apparatus and Auxiliaries — II

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Abstract No. and References

Leak Detection with a Mass Spectrometer Using Hydrogen Gas

42/II

Holland. A good leak detector should satisfy the following requirements: (1) leaks should be detectable during operation of the vacuum apparatus, (2) small as well as large leaks should be detectable and (3) the instrument should require 'clean' accessories only. Gases should be used for testing in preference to paints or liquids. Mass spectrometer methods appear to be the most sensitive of all methods known and helium the most suitable of all gases. As it is difficult to procure helium in Europe the use of hydrogen as a test gas was investigated. It was found that adverse background effects due to the presence of hydrogen ions originating from other sources were much less troublesome than originally expected and could be eliminated. In another series of experiments the following two performance characteristics of mass spectrometer leak detectors were studied: (1) the minimum size leak still detectable using various gases (see Table 2 reproduced below) and (2) the sensitivity of the method, if more than one leak is present.

Mass	*Test Gas*	*Smallest Leak Detectable*
2	Illuminating gas	0.8mm³/h N.T.P.
1	Illuminating Gas	2 mm³/h
2	Hydrogen	0.28mm³/h
1	Hydrogen	0.6mm³/h
2	Ether Vapour	2 mm³/h
1	Ether Vapour	50 mm³/h
4	Helium	1 mm³/day

Reference is made to the mass spectrometer fitted with a Philips ionisation-gauge type ion source, which facilitates the detection of leaks as small as 10^{-3}mm³/h N.T.P.

Sommaire: Détails d'une expérience utilisant le spectromètre de mass avec de l'hydrogène comme traceur.

Article by M. E. Reinders J. Schutten & J. Kistemaker *Appl. Sci. Res.* **B2**, No. 1. 1951 66-70

Vapour Pressure Measurements of Bromine

43/II

United Kingdom. The authors describe experiments concerned with the determination of the vapour pressures of bromine. Initially all measurements were taken with a silicone oil manometer but did not prove sufficiently accurate. Therefore, the experiments were repeated using a Pirani gauge fitted with a platinum filament.

Sommaire: L'auteur decrit des expériences sur la mesure de la tension de vapeur du brome.

Letter by J. Yarwood D. H. Le Croissette *Vacuum* **1**, Jan. 1951 37-38

Low Evaporation Rate Storage Vessel for Liquid Helium

44/II

United States. A four-litre spherical Dewar of conventional design employed by the authors for the storage of liquid helium was found to lose half its contents over night, even though the Dewar was immersed in liquid air. In an endeavour to improve this performance the authors studied the nature and mechanisms of conduction and radiation losses occurring in Dewar vessels and concluded that it is important to have adequate heat exchange between the cold vapour and the walls of the vessel, if the heat loss by conduction is to be kept small. A simple way to achieve this is to lengthen the neck of the vessel, thereby increasing the surface area available for heat exchange. To counteract radiation losses, lengthening of the neck of the Dewar vessel is suggested or, alternatively, the provision of a radiation shield at an appropriate level in the neck of the vessel. The authors describe a twelve-litre silvered spherical Pyrex Dewar vessel of their own design. Its inner walls extend several inches above the ring seal. The Dewar portion of the neck of the vessel is approximately twice as long as is usual in conventional Dewars. Finally, a stopcock is sealed onto the vacuum jacket to permit ready pumping away of the helium which has diffused through the Pyrex walls. A special method has been devised for filling the vessel. The new storage vessel was still half full ten days after filling.

Sommaire: Présentation de la théorie et de la performance practique d'une construction nouvelle d'un récipient Dewar.

Article by S. G. Sydoriak & H. S. Sommers Jr. *Rev. Sci. Instrum.* **22**, Dec. 1951 915-919

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III — Vacuum Processing Techniques — III

Abstract No. and References

30 — EVAPORATION — 30

The Production, Properties and Uses of Thin Films Condensed In Vacuo — 1/III

United Kingdom. The study of the properties of thin films deposited *in vacuo* has grown considerably in recent years. The vacuum equipment involves special design considerations, three major aspects of which are discussed: (1) evaporation pressure, (2) pumping speed and ultimate oil vapour pressures, and (3) the use of discharge techniques for the cleaning of contaminated supports. Applications are fully reviewed together with results of research work on structure and physical characteristics of films.

Sommaire: Le développement des appareils pour le revêtement sous vide nécessite des considérations spéciales qui sont discutées par l'auteur sous trois différents aspects: la pression requise, le débit des pompes et le nettoyage de la surface de base par un bombardement ionique.

Article by L. Holland *Vacuum* 1, Jan. 1952 23-36

'Evaporation Coating' Leathers — 2/III

See Abstract No.: 12/I

Vacuum Deposition — 3/III

See Abstract No.: 10/I

High Vacuum Metallising of Metals and Plastics — 4/III

United States. High vacuum metallising applied to metal stampings, die, sand and slush castings, extrusions, spinnings and turnings, is a comparatively new technique which may eventually replace electro-plating and silver-reduction plating in many fields. In a great number of cases processing costs of the new technique will prove to be lower than those of conventional methods. Certain operations such as buffing and wire brushing, hitherto an essential part of the production process, can be dispensed with altogether. The vacuum metallisation process consists essentially of three steps; (1) the application of an undercoat (lacquer) to the surface of the article to be metallised, (2) the deposition of the metal film and (3) the application of a top coat (lacquer). The choice of the right lacquer is important to ensure good adhesion of the metal film to the undercoat and good resistance to abrasion by the topcoat. A large part of the paper is devoted to the discussion of shop installations. By the way of example a complete shop lay-out and flow sheets are given covering an output of approximately 8,000 pieces /hr. of metal articles approximately $2\frac{1}{2}$ inches × $1\frac{1}{2}$ inches × 1 inch. Several of the components to be processed are fastened to a rod which is used as a work-carrying device through all stages of production. The actual deposition is carried out in a chamber which accommodates a fixture holding several of these rods and carrying some 10 to 20 individual filaments clamped to bars in the centre of the fixture. All rods are rotated during the evaporation process. The production arrangement described covers an area of approximately 2,500 square feet. A breakdown of the processing costs is added.

Sommaire: Revue des procédés de métallisation sous vide, donnant le schéma de circulation complet d'une installation de production.

Article by H. Hartman & M. Schneider *Metal Finish.* 49, Sept. 1951 64-70

Recent Advances in Vacuum Coating Plant and Techniques — 5/III

United Kingdom. Advances in the design of vacuum evaporation plant are shown by reference to a typical plant used for anti-reflection filming of lenses. Methods of removing surface contaminants by ionic and electron bombardment cleaning are reviewed. Recent industrial applications of vacuum coating, including the metallising of plastic foils and cathode-ray fluorescent screens, are described. (*Author*)

Sommaire: L'auteur décrit les développments récents en appareillage de vide et des techniques. Référence spéciale est faite au dépôt de films anti-réfléchissants sur des lentilles.

Article by L. Holland *J. Sci. Instrum.* Suppl. 1, 1951 59-62

A Multi-Electrode Ring for Vacuum Plant — 6/III

United Kingdom. A sketch and a short description are given of a multi-electrode ring for use in vacuum evaporation plant of conventional design. The ring is interposed between the rim of the bell jar and the base plate. In the case of an 18 inch diameter bell jar 12 electrodes can be accommodated on the ring, spaced some $4\frac{3}{4}$ inches apart. In this manner the number of electrodes can be increased without any structural alterations to the plant. The ring has proved useful in the course of experiments concerned with the deposition of multi-layer coatings.

Sommaire: Brève note concernant un anneau à insérer entre cloche et base d'un appareil à métalliser sous vide, qui doit servir de support à un grand nombre d'électrodes.

Note by K. M. Greenland *J. Sci. Instrum.* 28, Oct. 1951, 324

An Approach to the Microscopy of Molecules — 7/III

United States. It has been observed that the discontinuous distribution of particles in thin metal films produced by vacuum evaporation is subject to strong orienting effects. Reference is made to previous work on this subject by Levinstein, Lennard-Jones, and Sennett and Scott. The author illustrates this phenomenon

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in a number of micrographs attached to the article. On deposition the atoms tend to agglomerate on the surface in units of circular shape. This circular formation can be explained by the fact that the binding of one metal atom to another is large compared with the binding of the metal atom to the organic material, composing the substrate. At a later stage these units tend to link and form a linear bead-like pattern. It is now clear that this latter formation is due to the influence of the structure of the substrate material and in particular to the linear molecules in this material. In order to clarify this condition nitro-cellulose separated into groups of uniform polymer lengths was dissolved in amyl-acetate and thin substrate films formed from the solution. Gold and silver films between 10-20 Å in thickness were deposited on to this substrate and showed a distinctly linear formation dependent on the polymer length of the substrate. It appears that this technique could be useful if applied to the investigation of molecular lengths in the range of 100 to 1,000 Å.

Sommaire : Etude de la relation de la structure du support avec la structure du film métallique déposé. Il est suggéré que la technique de métallisation par évaporation sous vide pourrait faciliter l'étude des longueurs moléculaires dans la région 100-1,000 Å.

Paper by M. S. Blois, Jr. *Science* 114, 17.8.51. 175-177

Surface Treatment of Lenses

8/III

United Kingdom. H. D. Taylor of York, the designer of the Cooke Triplet photographic lens (1896) was the first to discover that tarnishing of glass surfaces increases the transmission of light through the lens and at the same time reduces the reflection of light from the surface. Gershun in Russia and F. E. Wright in the U.S.A. studied this phenomenon during the period of the First World War. But not until 1935 was a proper method developed for the production of an anti-reflection layer of low refractive index on a glass surface (J. Strong). Today, there are three methods available for the production of such coatings; (1) the leaching process, (2) the spinning process and (3) the vacuum coating process. Untreated lenses reflect up to 5% of the incident light at the air-to-glass surface. After treatment this figure is reduced to 1% and the transmission increased to 98.8%. Absorption accounts for 0.2%. The layers are usually formed from magnesium-fluoride or cryolite and should have the thickness of approximately a $\frac{1}{4}$ of the wavelength of the light transmitted. The refractive index should be approximately equal to the square root of the index of the glass treated. If light strikes a coated lens, light waves are reflected from the surface of the coating and from the surface of the actual lens. The second set of reflected waves will be out of step with the first because the light has travelled further. If the two sets are out of phase by a fraction of one wavelength, the reflections will interfere with each other and under optimum conditions cancel each other. As a result the over-all reflection will be reduced and the energy originally constituting the reflected light will now reinforce the transmitted light. Details are given of the vacuum evaporation method for the prepartion of anti-reflection films.

Sommaire : Discussion de la théorie de la reduction de la réflexion par le 'blooming' des lentilles. Les méthodes produisant de telles couches sont discutées.

Article by J. Adams *P.D.A. Journal* Sept. 1951 28-33

Density Control in the Manufacture of Rhodium Filters

9/III

United Kingdom. The author comments on difficulties encountered when producing rhodium filters of low optical density :—(1) After completion of the deposition process, the density value of the filter continues to increase for an appreciable time before stability is reached. (2) Burnishing changes the value of density finally arrived at. (3) In the case of small filters, the reduced density near the border of the filter has an appreciable effect on the average density of the filter.

Sommaire : Les difficultés sont discutées qui se sont présentées dans la fabriquation des filters en rhodium à faible densité optique.

Letter by W. Zehden *Vacuum* 1, Jan. 1951 38-39

On the Production of Diffraction Grating—I. The Copying of Plane Gratings

10/III

See Abstract No. : 28/I

Observations on the Metallisation of Surfaces by Evaporation in a Vacuum

11/III

France. The author discusses the cleaning of supports for the deposition of metals by evaporation *in vacuo.* He refers to the conventional procedure by ionic bombardment and points out that cleaning by this method is not always satisfactory. As an alternative he suggests bombardment by electrons produced by thermionic emission. He gives details of a suitable arrangement and advice on its use. Discussing filaments used as crucibles he remarks that he found tantalum more satisfactory than tungsten. Tantalum filaments stay malleable where tungsten becomes brittle.

Sommaire : Un aperçu des avantages que présentent les méthodes de bombardment electronique appliquées au nettoyage de supports à métalliser sous vide. On fait aussi remarquer que le tantale peut parfois remplacer avantageusement le tungstène comme matériau de creuset.

Note by L. Dunoyer *C.R. Acad. Sci. Paris* 233, No. 17, 1951 919-921

Contamination of Evaporated Films by the Supporting Material of the Source

12/III

See Abstract No. : 33/I

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Contd.

Abstract No. and References

Effects of the Evaporation Technique on Optical Glass

13/III

Australia. Professor Tolansky mentioned in his article (*Vacuum,* 1, page 75) that permanent damage to glass or quartz optical glass sometimes occurs during cathodic sputtering of a metal onto the surface. The author reports that he made similar observations when evaporating silver on to optical flats. In one case, a nodulation of 1-2 λ had formed on the glass.

Sommaire : Le Professeur Tolansky fit remarquer dans un article publié dans ce journal, qu'il avait observé que des surfaces en verre étaient parfois détériorées pendant la déposition d'un film métallique. L'auteur signale une observation semblable.

Letter by C. F. Bruce *Vacuum* 1, Oct. 1951 300-301

Notes on the Coating of Plastic Foils

14/III

United Kingdom. The author comments on the article by L. Holland and the letter of W. Zehden published in the first issue of *Vacuum.* He records his own experiences with ' plastic ' films as substrates for evaporated coatings. These supports tend to stretch and tear due to the radiant heat emitted by the evaporation source. Suggestions are made on how to overcome these difficulties.

Sommaire : L'auteur a fait l'observation que des supports ' plastiques ' ont souvent tendance à s'étirer et à se déchirer par suite de la chaleur radiante de la source d'évaporation et donne connaissance des mesures à prendre pour réduire sensiblement cet inconvénient.

Letter by T. A. J. Jaques *Vacuum* 1, April 1951 115

Photo-Conductivity in Vacuum-Coated Selenium Films

15/III

United States. The dark resistivity of selenium films is good enough to justify their use as photo-conductive layers in electro-photography. A method is described of depositing vitreous selenium at base plate temperatures of less than 50°C. Such films possess sensitivity in the blue and green range only. To obtain sensitivity in the red special measures have to be taken. The overall sensitivity can be increased by the addition of tellurium.

Sommaire : Description d'une méthode pour obtenir la sensibilité dans le spectre bleu, vert et rouge pour les couches de selenium photo-conductives déposés sous vide.

Abstract P. H. Keck *J. Opt. Soc. Amer* 41, Nov. 1951 871

A Photo-Conductive Effect in Tellurium Films

16/III

See Abstract No. : 31/I

Method of Preparing Skiatronic Screens

United States. A method is proposed for the improvement of the performance of ' dark trace ' tubes by increasing the contrast of the dark traces with respect to the background. The quality of the contrast depends largely on the quality of the potassium chloride film applied to the tube walls. The method provides for the deposition of two layers of potassium chloride in two consecutive steps. The first step comprises the deposition of a halide film by vacuum evaporation in the presence of nitrogen or air at a pressure of 20-60 micron Hg. This deposit is completely transparent. The second layer is evaporated on to the first at a pressure of about 0.1 micron Hg. The result is a white translucent coating. An alternative procedure is described whereby the second layer is deposited in the presence of water vapour at a pressure of 4.6 to 9.5 mm. Hg. The latter treatment has the effect of increasing the period of decay or persistence of the dark trace.

Sommaire : Ce brevet s'applique à un procédé pour le dépôt de films de chlorure de potasse par évaporation sous vide en deux stades consécutifs ayant pour but d'améliorer la performance des tubes électroniques du skiatron type.

G. R. Fonda *U S. Pat.* 2,545,200

Electrical Properties of Thin Layers of Germanium

18/III

Abstract No. : 19/I

A Possible Explanation of the Increase of the Electrical Resistance of Thin Metal Films at Low Temperatures and Small Field Strengths

19/III

Holland. Van Itterbeek *et al.* established that the electrical resistance of certain metal films increases considerably at low temperatures and that the resistance value is dependent on the voltage drop in the film, a fact which is particularly pronounced at small field strengths. It has further been found that the resistance does not become constant at small field strengths, therefore this phenomenon cannot be attributed to Joule Heat effects, tunnel effects or semi-conductor phenomena. It has been suggested that thin films consist of separate grains or blocks and the author investigates whether the rise of resistance can be explained by the peculiar conditions arising from electrons passing through such a system of grains or blocks. It can be assumed that at very low temperatures the relative number of positively and negatively charged grains will remain small as long as the electrostatic energy of one pair of charges is large compared with the thermal energy (kT). But as transitions of electrons occur this electrostatic energy will increase and the distance between the positive

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and negative charge lengthen. If an electric field is applied at this stage, only those charges will contribute to the electric current which can escape the electrostatic attraction of their partners. Clearly at small field strengths the number of charges escaping will be small. Certain calculations are added evaluating this effect.

Sommaire : On soumet une explication de l'accroissement de la résistance électrique des lames minces métalliques à basses températures.

Article by C. J. Gorter *Physica* 17, Aug. 1951 777-780

Contact Potential Variations on Freshly Condensed Metal Films at Low Pressures 20/III

United States. Work function is defined as the minimum energy required to liberate an electron from the surface of a metal at O°K. The potential barrier which the electron has to pass is created by the discontinuous array of positive ions at the surface. This discontinuity is eliminated if two metals are brought into electrical contact and electrons are exchanged freely. On contact, the difference in affinity for electrons between the two metals concerned effects a net shift of charge, until the potential difference between them becomes equivalent to the difference in work functions. This difference of potential is termed the ' contact difference of potential ' and can be measured electrostatically. The presence of adsorbed or chemically combined atoms or molecules on the surface changes the work function of the pure metal surface appreciably. In this investigation aluminium, copper, gold, nickel. iron and chromium films were deposited on a support which, after completion of the evaporation process but still *in vacuo*, was placed into a position facing a platinum plate (platinum being used as the reference material), the two plates forming a condenser. With the test film in position the effects of progressive oxidation on the work function could be observed and recorded by a series of electrical measurements at various sub-atmospheric pressures. The behaviour of the aluminium surface was different from that of the other metals. It showed a great initial affinity for oxygen and a tendency to be covered rapidly by a monolayer of oxygen molecules. After this initial decrease the value of the work function showed a certain stability at low pressures. At higher pressures the value of the work function increased. The probable mechanism of progressive oxidation is discussed. It appears that this experimental method offers a powerful tool for the study of oxidation phenomena on metal surfaces.

Sommaire : Des mesures de potential de contact ont été faites sur des films de cuivre, or, nickel, fer et chrome, déposés sous vide. Ces mesures offrent un moyen efficace pour l'étude des effets d'oxydation sur des surfaces métalliques.

Article by L. L. Antes & N. Hackerman *J. Appl. Phys.* 22, Dec. 1951 1395-1398

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Cathode Coatings 21/III

See Abstract No. : 22/IV

The Reaction Between Deuterium and Ammonia on Evaporated Metal Catalysts 22/III

See Abstract No. : 51/I

Activated Adsorption of Hydrogen on Nickel Catalysts 23/III

See Abstract No. : 49/I

Evaporation of Silica 24/III

Austria. The author reports on the methods used in his laboratory for the production of quartz coatings with good adhesion properties by means of vacuum evaporation. It has been found virtually impossible to evaporate SiO_2 without causing at least partial reduction to SiO. The author observed also that all refractories used as materials for crucibles attack silica in certain temperature ranges. The oxygen thus liberated promotes oxidation of the crucible material which effects, indirectly, a contamination of the deposit. If proper precautions are taken the adhesion of the films is not affected.

Sommaire : L'auteur rend compte des méthodes employées dans son laboratoire pour la production de dépôts de quartz, ayant de bonnes propriétés d'adhésion, par le procédé d'évaporation.

Letter by A. de Rudnay *Vacuum* 1, July 1951 204-205

A Simple Process for the Production of Transparent Foil of Great Surface Area in Thicknesses Varying from 50 to 300 mμ. 25/III

Germany. Transparent foil of a thickness varying from 50 to 300 mμ was required for a certain experiment. Collodion foil could not be used as this material was not sufficiently heat and corrosion resistant. The author decided to use unsupported oxide foil for the purpose. Hass and Kehler were the first to produce unsupported oxide films for electron microscope work. Their method was similar to that employed in the production of electrolytic condensers. In preparing the foil the author followed closely the procedure of Hass and Kehler modifying it where necessary to obtain strips of foil of the required size. The edges of a piece of pure aluminium foil 10 to 15 μ thick were treated in an electrolytic bath containing 3% ammonium citrate. Subsequently, the centre section of the aluminium foil was oxidised in the same way. The current was maintained at 0.3 amp. throughout the treatment, the voltage was 160. The thickness of the oxide film was found to be a function

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of the voltage (13.7 Å p. volt). After completion of the oxidation the aluminium foil carrying the oxide deposit was exposed to the fumes of hydrochloric acid which caused the aluminium to dissolve in a few minutes. After rinsing and drying the oxide foil was ready for use. Unsupported oxide films of an area up to 4 × 5 cm² can be produced by this method. See Abstract 26/III.

Sommaire : Description d'une méthode pour la production de films d'oxyde d'aluminium sans appui d'une dimention allant jusqu'à 4 × 5 cm² et d'une épaisseur d'environ 2.000 A.

Note by K. Strohmaier *Z. Naturforsch.* 6a, Sept. 1951 508-509

The Refractive Index of Thin Al_2O_3 Films

26/III

Germany. The refractive indices of oxide films produced by the method described in Abstract 25/III were determined by the immersion method. The films varied in thickness from 1,233 to 2,740 Å. Thicker films could not be produced by the same method at room temperature and thinner films would not stand up to the testing procedure. The results of the measurements carried out with sodium light are embodied in a table which is reproduced below. The reason for the variation in the values of the refractive index in not clear. Various tentative explanations are given.

Voltage Applied in the Production of the Film	*Refractive Index*
90	1.567
100	1.573
110	1.576
120	1.582
130	1.587
140	1.590
150	1.592
160	1.596
170	1.601
180	1.603
190	1.611
200	1.614

Sommaire : Après mesurage des films d'oxyde d'aluminium pour établir leur index de réfraction on en donne les résultats sous forme de table.

Note by W. Weiskircher *Z. Naturforsch.* 6a, Sept. 1951 509

31 — CATHODIC SPUTTERING — 31

The Production, Properties and Uses of Thin Films Condensed In Vacuo

27/III

See Abstract No. : 1/III

36 — DRYING — 36

The Theoretical Factors of Vacuum Drying

28/III

France. In order to establish a theoretical basis for vacuum drying techniques the author has studied methodically all factors which may influence the rate of evaporation of water from the liquid or frozen state. He used an ampoule filled with water, immersed in a liquid bath and connected through a pipe line to an evacuated condenser. Some of the factors investigated were : the latent heat, the vapour pressure, the thermal conductivity of the ampoule material, the conductance of the pipe line from ampoule to condenser, the initial temperature of the water and the temperature of the bath. Simple formulae are given which permit the determination of all relevant factors.

Sommaire: Une étude approfondie de la théorie du séchage sous vide à la lumiere de l'étude des facteurs régissant l'évaporation de l'eau à l'état liquide ou congelé.

Article by L. Dunoyer *Le Vide* 6, July-Sept. 1951 1025-1040 and 6, Nov. 1951 1077-1090

Large-Scale Vacuum Dehydration

29/III

United Kingdom. Vacuum dehydration on a large scale is a comparatively recent development. The technique utilises the fact that under reduced pressure, liquids boil at lower temperatures. For instance, at a pressure of 4.6 mm. Hg water boils at 0°C and at 0.034 mm. Hg it boils at -50°C. These facts form the basis of the freeze drying process. The article deals mainly with the drying of liquids in the millimetre range, a process applied on a large scale in the food industry. Its main purpose is the reduction of the moisture content without thermal decomposition or oxidation of the processed material. Secondary considerations are the reduction in bulk for transporting and storage. The principle parts of a vacuum dehydration plant are the vacuum evaporator and the pumping and vapour absorption system. Various vapour pumping systems are discussed in detail. Falling-film drying techniques are mentioned as applied to the concentration of fruit juice, for instance. A complete flow diagram of the so-called Florida process for the drying of orange juice is given. Finally belt dryers are described developed in the U.S.A. recently and providing for a horizontal conveyer

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belt in a vacuum chamber, on to which the material to be dried is sprayed. The solution sprayed on to the belt is pre-concentrated and therefore dries rapidly. It clings in the form of a froth to the underside of the belt from which it is scraped off and collected in a removable container through an air lock. A plant of this type was first used for the production of coffee extract; it may find application for continuous freeze drying.

Sommaire : La concentration de liquides sous vide est discutées, en particulier quant à son application à l'industrie alimentaire.

Article by D. R. Goddard *J. Sci. Instrum.* Suppl. 1, 1951 43-46

Evaporation in Low Vacuum from Warm Granular Material (Wheat) During the Falling-Rate Period

30/III

United Kingdom. A comprehensive study of the influence of pressure, temperature and moisture content on the rate of drying of wheat in vacuum. Manitoba and English wheat were tested. All details are given of the experimental arrangement and procedure. In the majority of cases measurements were taken at a constant pressure i.e. 7 mm. Hg. Each sample was treated for 20 minutes. The initial moisture content of the material varied from 12 to 23%, its temperature from 23 to 46°C. It has been stated by other workers that, in the case of ordinary air-drying, the rate of evaporation of water increases as the temperature rises and, for low atmospheric humidities, is roughly proportional to the saturation pressure at any given temperature. The present study seems to confirm the existence of a similar relationship in vacuum drying. The rate of drying is strictly proportional to the moisture content during the falling-rate period just as in air-drying. It can be assumed that, processing at moderate temperatures, the drying rate of wheat is limited by the amount of water ' bound ' in the grain and can only be increased by raising the grain temperature. The shape of the drying plant may cause considerable impedance to the vapour movement and reduce the drying rate, in particular at higher pressures. This can be effectively counteracted by the provision of air sweeps in the drying system. The results of an experiment to prove this are shown in tabular form reproduced below. By the admission of a volume of air equal to $\frac{1}{8}$ of the volume of water vapour formed in the process the drying rate could be doubled, but it could not be improved any further when the volume of admitted air was equal to that of the vapours formed.

TABLE II

Effects on loss of moisture during 20 *minutes of different rates of admission of air into* 50 *g. wheat at* 30°*C. under reduced pressure* (*wheat was Atle English at* 18% (21.9%) *initial moisture content*)

Rate of Admission l./hr. of Air at Atm. Pressure	*Press. in System cm. Hg.*	*Loss % of Initial Wt.*	*Loss % of Dry Wt.*	*Ratio Vol. Water Vapour. / Vol. Air*
Nil	3.6	0.98	1.2	—
1	3.5	1.71	2.09	3.4
2	3.8	1.76	2.15	1.8
3	3.7	1.95	2.38	1.3
4	3.7	2.15	2.62	1.1
5	4.5	2.16	2.64	0.9
9	6.0	2.18	2.66	0.5

Sommaire : Compte rendu sur des essais faits en vue d'établir les avantages de la dissécation sous vide de matières granulées (blé).

Article by C. R. Jones *J. Sci. Food Agric.* **2**, Dec. 1951 565-571

Frozen Concentrated Apple Juice

31/III

United States. The Eastern Regional Board Laboratories have developed a method of manufacturing frozen concentrated apple juice for sale in the Eastern market, where non-depectinised apple juice is preferred by the consumer. The method consists of the following steps : preparation of the juice, recovery of the essence, clarification, concentration of the stripped juice, addition of the essence, filling, packing and freezing. The process is similar to, but in part deviates from, the so-called Florida process applied in the production of citrus juice. Concentration is carried out at a higher pressure, *i.e.*, 26 inches. Also, the new process employs conventional methods for essence concentration. Methodic experiments had been carried out previously on the influence of pressure applied during concentration on the taste and other qualities of the product in general, by performing the process experimentally under a pressure of 26, 27.5 and 28.5 inches Hg, boiling the juice at 120, 104 and 85°F respectively. But no difference could be detected. Details are given of the capital expenditure and running cost involved converting an apple processing plant with an output of 417 gallons of juice per hour into a frozen concentrate plant. The saving of cost in containers over those required for bottled juice will cover almost the total additional processing cost.

Sommaire : Détails d'un nouveau procédé de fabrication de jus de pommes frais concentré. Détails sur le capital engagé et les frais d'exploitation engendrés dans une telle installation.

Article by R. K. Eskew G. W. Macpherson Phillips R. P. Homiller C. S. Redfield and R. A. Davis *Industr Engng. Chem.* **43**, Oct. 1951 2397-2403

Rapid Heat Processing of Fluid Foods by Steam Injection

32/III

See Abstract No. : 60/III

Vacuum Flash Evaporator Removes Volatiles from Oils

33/III

United States. A short description is given of a new type of vacuum flash evaporator which has already been used over a considerable period for the dehydration of lubricating and transformer oils. The pre-heated feed is introduced into a rotor which atomises the liquid and projects it into a zone of reduced pressure. Dis-

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solved gases and low boiling liquids flash quickly into the vapour space and are withdrawn through the vacuum system. The operational pressure is 28 inches. The standard units are made in 4, 6 and 8 feet diameter and are rated in terms of water evaporated when dehydrating oil at 187.5, 375 and 750 pounds/hr.

Sommaire : Description d'un nouveau type d'évaporateur instantané, recommandé pour la déshydratation d'huiles de graissage et de transformatuers.

Note by Anon. *Chem. Engng.* 58, Oct. 1951 177

Vacuum Drying of Electrical Insulation in the Service Shop

34/III

United States. Excessive amounts of moisture absorbed by the electrical insulation material will reduce the service life of electrical equipment. The problem of drying is not only of importance during the manufacture of apparatus but also in connection with servicing and repairs. A moisture content of a few % may result in condensation within the apparatus. While repairs are being carried out an appreciable moisture pick-up is taking place and necessitates re-drying. The highest permissible temperature employed in drying is approximately 100°C. Drying can either be carried out in a fast air stream circulating at a velocity of about 200 ft./min. or in a vacuum. Pressures used in vacuum drying are in the range of 29-30 inches. Details are given of a complete drying cycle for a medium size transformer. During the heating-up period air is circulated until the temperature of the hottest point within the transformer reaches approximately 70°C. Then the air circulation is turned off and vacuum applied for an hour using the heat radiating from the walls only. Subsequently air is again circulated until the temperature has risen to 80°C, when the vacuum cycle is repeated. This procedure is continued until a temperature of 100-105°C is reached. At this stage full vacuum is applied for about 8 hours. The progress of drying can be followed by measuring the insulation power factor. The value of the insulation power factor rises with temperature. When the temperature is constant the values measured should decline as moisture is being removed until they reach a steady low value indicating that drying is complete. Details of the equipment required are given.

Sommaire : Discussion des méthodes à employer et de l'équipement à utiliser pour le sèchage de l'isolant dans des appareils életriques d'envergure, tels des transformateurs après réparation.

Article by N. R. Maleady *Gen. Elect. Rev.* 54, Aug. 1951 52-54

37 — METALLURGICAL PROCESSES — 37

Vacuum Metallurgy—Its Characteristics and Its Scope

35 III

United States. The actual and potential uses of vacuum methods in metallurgy are discussed. The author makes a general examination of conditions in metallurgical processes carried out in vacuum. He then proceeds to survey existing furnace designs, their performance and limitations. Finally, he describes a large variety of metallurgical procedures, where the application of vacuum would appear to offer advantages.

Sommaire : Les méthodes utilisants le vide actuellement employées en métallurgie et celles qu'il serait possible d utiliser sont discutées.

Article by W. J. Kroll *Vacuum* 1, July 1951 163-184

Comments on Catalytic Aluminium Distillation

36 III

United Kingdom. The author refers to statements made by Dr. Kroll in his article (*Vacuum*, 1, 176-177) on procedures for the production or refining of aluminium. He gives the details of the two procedures concerned, aiming at clarifying certain points mentioned in the article. In his reply, Dr. Kroll confirms that the comments made by the author of the letter are correct.

Sommaire : L'auteur de cet lettre examine certaines assertions de Docteur Kroll dans son article sur la Métallurgie Sous Vide (*Vacuum* 1, 173-177). Réponse de Dr. Kroll à cette critique.

Letter by P. Gross *Vacuum* 2, Jan 1952 56

Titanium—1951

37 III

See Abstract No. : 56/I

Dollar-a-Pound Titanium

38/III

Japan. A short description is given of a new method of producing titanium from iron sand deposits available in Japan. The process consists basically of four operations: (1) Reduction of iron sand in an electric furnace yielding pig iron and titanium bearing slag. (2) Chlorination of the slag yielding titanium tetrachloride. (3) Purification of the titanium tetrachloride and (4) reduction of the titanium tetrachloride with magnesium and vacuum distillation resulting in metallic titanium. Applied on a laboratory scale the process yielded titanium of 99.5% purity. It is claimed that application of this process on a 100-ton-per-month scale in a plant near to an adequate power source would eventually reduce the price of titanium to a figure below $1 per pound.

Sommaire : Brève description d'une méthode nouvelle de production de titanium à partir de gisements de sables ferrogineux du Japon.

Note by Anon, *Chem. Engng.* 58, Nov. 1951 278

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The Hot-Wire Process for Zirconium

39/III

United States. In order to understand better the hot-wire process for Zr, a study has been made of the thermal decomposition of Zr tetraiodide molecules which are isolated from the effects of interaction with other tetraiodide molecules and with the reaction products. It was found that the probability that a given Zr-tetraiodide molecule will decompose upon striking once upon a hot surface *in vacuo* is very high, approaching unity at 1,400°C. This work was supplemented and extended by a second series of investigations, which were based upon pressure measurements made inside of an operating cracking bottle. From these two experimental approaches considerable information was gained about the hot-wire process, including the knowledge that the rate-determining step is that of gaseous transport, and that the initial synthesis of Zr tetraiodide in the cracking bottle is catalysed, apparently photochemically, by the lighting from the filament.

(*Nuclear Science Abstracts*)

R. B. Holden & B. Kopelman *Atomic Engy. Comm. Rep.* SEP.-58 (X) (rev.), June 1951

Sommaire : Compte rendu de travaux de recherche sur la performance du processus de fils de fer a chaud pour la production de zirconium.

High Purity Metal

40/III

United States. Details are given of a procedure to prepare pure zirconium low in hafnium content. Commercially available zirconium usually contains approximately 3% hafnium. The separation of hafnium from zirconium is extremely difficult. It was achieved by fractional distillation of a mixture of zirconium tetrachloride and phosphorus oxychloride resulting in zirconium oxide. The purified oxide was chlorinated in an apparatus which is shown diagrammatically and operates in a vacuum produced by a water jet pump. The zirconium tetrachloride thus obtained was converted to zirconium sponge in a reducing unit which consisted of a sublimation chamber having an iron product pot underneath. The zirconium tetrachloride was placed in the sublimation chamber and sodium in the product pot. The unit was evacuated to 20 inches Hg pressure and backfilled with helium prior to use. The sodium heating up in the product pot reacted with the tetrachloride evolving from the sublimation chamber. Sponge thus obtained was converted to high purity zirconium in a de Boer-type iodide decomposition tube. This latter reaction took place in a vacuum of about 10^{-5}mm. Hg. Approx. 9% (by weight) of the quantity of zirconium oxide used for this procedure was recovered in the form of pure zirconium. Table I reproduced below gives the composition of the metal after each stage.

Element	*Purified* ZrO_2	$ZrCl_4$	*Sponge*	*Iodide Zirconium*
ZrO_2*	92 to 97			
Zr			99.52†	99.93†
P_2O_5	1.35 to 4.56			
Al	0.02 to 0.07	0.014	0.037	<0.003
Ca	0.005 to 0.044	0.006	0.007	<0.003
Cu	0.003 to 0.014		0.004	
Fe	0.005 to 0.035	0.019	0.115	<0.003
Mg	0.004 to 0.012	0.012	0.185	<0.003
Ni	0.008 to 0.027	0.011	0.008	0.008
Si	0.004 to 0.173	0.025	0.072	0.017
Ti	0.003 to 0.007	0.004	0.004	<0.003
Hf	0.007 to 0.042	0.028	0.028	0.029

* Determined by wet analyses † By difference

Sommaire : Bref rapport sur un procédé de préparation de zirconium à basse teneur en hafnium.

Article by F. B. Litton *Metal Prog.* 60, Dec. 1951 83-86

Applied Vacuum Metallurgy—The Production of Magnesium, Calcium, Tantalum and Zirconium

41/III

United Kingdom. The use of vacuum in the production of specific metals on an industrial scale is described. Details of the process used for the production and treatment of magnesium, calcium, tantalum and zirconium are given. The work described indicates that the improvements in vacuum equipment together with the experience which has been gained by metallurgical engineers will lead to a rapid development of vacuum metallurgical techniques.

Article by G. L. Miller *Vacuum.* 2, Jan. 1952 19-32

Sommaire : Détails des procédés utilisés pour la production et le traitement du magnésium, du calcium, du tantale et du zircon.

Production of Ductile Vanadium by Calcium Reduction of Vanadium Trioxide

42/III

See Abstract No. : 59/I

An Introduction to Arc-Cast Molybdenum and Its Alloys

43/III

See Abstract No. : 60/I

Molybdenum A New High Temperature Metal

44/III

See Abstract No. : 61/I

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Abstract No. and References

Melting and Sintering of Metals In Vacuo

45/III

United Kingdom. The absence of air in metal sintering, purifying, heat treatment or casting processes results in a product with lower gas content, greater activity and toughness, higher density, freedom from blow holes and improved electric and thermal conductivity values. Gas can dissolve in a metal either by forming a simple solution or by forming a compound with the metal. In the first case the amount of dissolved gas is determined by $Q = Kp^{\frac{1}{2}}e^{T}$, where K is a constant, T the temperature and p the gas pressure over the metal. Typical for the second case is oxygen contamination giving the metal oxide. The dissociation pressure p of the oxides and the dissociation temperature T are related by log p = A-B/T, where A and B are constants. For iron oxide, for instance, the dissociation pressure is 10^{-5}mm. Hg at 1,550°C. A temperature of 2,500°C is required to raise this pressure to 1 mm. as would be required in a vacuum furnace to provide for an effective reaction towards lower oxygen content. In sintering one has to deal with three types of gases which may be present in the pores of a sinter: (1) gases which dissolve in the metal, (2) gases which diffuse through the metal and (3) gases which neither dissolve nor diffuse through the metal. All three combine in slowing down the ordinary sintering process. By sintering *in vacuo* the effects of all three types of gases can be reduced by a factor of about 10^4. Details are given of a vacuum furnace which is high-frequency heated and designed to handle melts of 50 to 100 lbs. of a non-magnetic steel alloy. It is advisable not only to melt the material in vacuum but also to cast the ingot in vacuum. Various designs facilitating bottom pouring or tilt pouring in vacuum are described and shown in illustrations.

Article by E. D. Malcolm *J. Sci. Instrum.* Suppl. 1, 1951 63-66

Sommaire: Théorie et pratique de la fusion sous vide, la fonderie et le frittage de métaux, sont données, suivis de la description détaillée d'un four à vide.

A High-Temperature Vacuum Induction Furnace

46/III

United States. Details are given of a furnace which has been developed specially for the purpose of measuring the viscosity or other physical properties of ceramic materials at high temperature. An important requirement was the attainment of temperatures beyond 2,000°C and the maintenance of the same for a period long enough to facilitate proper readings and observations. The furnace consists of a water-cooled brass shell 5 inches in diameter, $\frac{1}{8}$ inch thick and 18 inches long. The cooling tube is soldered to the shell in the form of a widely spaced helix. The top and bottom plates of the furnace are removable and sealed with silicone rubber gaskets. The heat is supplied by a high-frequency generator with an output of 10 kw at frequencies from 200 to 600 kc. The inductor coil is led into the furnace through compression rubber fittings. The susceptor tube—the actual heating element—is made from molybdenum but as this material tends to evaporate at very high temperatures tantalum is preferable. The susceptor tube is fitted inside a fused silica cylinder which in turn fits closely inside the inductor coil. Tungsten-molybdenum thermocouples are used for temperature measurements but have not proved fully satisfactory. The operational pressure is 1 μ Hg or better and is produced by an oil diffusion pump coupled with a mechanical fore pump. The required vacuum can be obtained within 30 minutes.

Article by H. T. Smyth R. H. Meinken & L. G. Wisnyi *J. Amer. Ceramic Soc.* 34, May 1951 161-163

Sommaire: Détails d'un mouffle construit spécialement dans le but de mesurer la viscosité ou d'autres propriétés physiques de matériaux de céramique aux températures élevées.

An Improved Vacuum Fusion Furnace

47/III

United States. The presence of gases in combination or in solutions, even in minute quantities, may greatly affect the physical properties of metals. For instance, a consignment of nickel to be used for vacuum valve-cathodes was found to contain oxygen of the order of 0.008 to 0.02%. This amount can seriously impair electron emission. To determine the amount and kind of gases present in a metal the vacuum fusion furnace method is usually employed. A specimen of the metal is melted in a graphite crucible by means of a high-frequency induction cell. Oxides are reduced by combining oxygen with carbon and the resulting CO together with other liberated gases is pumped off for analysis. The success of this process very largely depends on the design of the furnace. When only small samples of the order of 1 gram or less are available, this method often lacks precision and reliability. A vacuum furnace is described here which gives good results from small samples. It essentially consists of a quartz tube, 2 inches in diameter and 6 inches long, suspended from glass hooks by means of platinum wires inside a Pyrex glass envelope of 3 inches diameter. The quartz tube contains a graphite crucible resting on graphite powder loosely packed to retain the heat generated in the crucible and also to permit the free flow of gases to be pumped out. The crucible is $\frac{3}{4}$ inch in diameter and 3 inches long. It is provided with a graphite funnel which is split lengthwise to avoid eddy-currents. An opening at the bottom of the outer glass envelope facilitates the insertion and removal of the quartz tube and associated components. Samples of the metal to be studied are admitted to the furnace through a branch tube connected to a group of sealed tubes, where up to 12 samples can be stored. Ferrous samples are moved from the storage tubes to the furnace by manipulating a small magnet outside and non-ferrous samples are stored in little cups made from magnetic material which can be suitably shifted and unloaded in the same way. This arrangement makes it possible to study several samples without breaking the vacuum seal. The temperature is measured by an optical pyrometer. Evacuation is carried out by a 2-stage mercury diffusion pump coupled with a mechanical fore pump. The furnace has been used for determinations on iron, molybdenum, copper, germanium, microphone carbon and nickel, during the last two years. Samples as small as 0.1 gram have been employed.

Article by W. G. Guldner *Bell. Lab. Rec.* 29, Jan. 1951 18-20

Sommaire: On décrit en détail un nouveau four de fusion sous vide, permettant l'emploi de très petits échantillons, jusqu'à un minimum de 0.1 gramme

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Abstract No. and References

Metallography at Elevated Temperatures 48/III

See Abstract No. : 53/I

38 — DISTILLATION — 38

Evaporation from Liquid Surfaces in Vacuum 49/III

United States. The best rate at which a liquid can evaporate is generally unimportant at atmospheric pressures because distillation is conveniently done thousands of times more slowly. In the high vacuum still the optimum rate is the one that limits yield of distillate and thus assumes first importance. Previous investigations have suggested that *evaporation coefficients* ranging from 1-25 per cent. of those calculated by the Knudsen-Langmuir formula are common. Only mercury and carbon tetrachloride have shown coefficients of unity. The authors experiments were predicated on the theory that the liquids, irrespective of constitution, will show coefficient of unity from new, clean surfaces and that the same liquids in the state of out-of-the-bottle purity or less will show fractional coefficients. This proves to be the case. The clean surface experiments were done with a falling-stream rate tensimeter, the soiled surface with various observation-post pot stills. When the equilibrium pressure is above 10 microns a soiled surface becomes SCHIZOID, divided into WORKING and TORPID areas. The working area has a coefficient near unity, the torpid two to one hundred times less. An expanding surface, as in a growing bubble, has a higher co-efficient than a contracting surface and more vapour is emitted behind a stirring paddle than in front. A technique has been devised for making exact measurements of vapour emission from stretched and pushed surfaces of known age and purity. As the surface reaches PRISTINE cleanliness, the evaporation coefficient becomes unity and does not diminish with later ageing of surface. Pristine surfaces are not ordinarily encountered, and proneness to superheat is an indication of the impaired permeability of a liquid surface.

Sommaire : Une étude fondamentale et détaillée des phénomènes observés en matière d'évaporation de surfaces liquides sous vide.

Article by K. Hickman & D. J. Trevoy *Vacuum* **2**, Jan. 1952 3-18

Low Pressure Distillation 50/III

Germany. Ordinary vapour distillation, molecular distillation and unobstructed path-distillation are discussed with particular reference to the treatment of high-boiling temperature-sensitive materials. Ordinary column stills are operated in a pressure range down to 1 mm. Hg. The remaining two methods are operated at lower pressures, *i.e.*, in the range from 1 to 10^{-5}mm. Hg. In the case of molecular distillation the still is evacuated to a pressure of 10^{-3}mm. Hg or less in order to ensure a mean free path of the residual gases which is larger than the distance between evaporator and condenser face. As a result the vapour molecules of the distilland very rarely collide with molecules of the residual gas and are not reflected back on to the evaporator surface. The efficiency of this method is governed by the (low) vapour pressure of the distilland. Where the processed material can be exposed to somewhat higher temperatures: unobstructed path distillation is preferable. Basically this method is the same as that of molecular distillation except that the pressure of the evaporated material is greater than that of the residual gas by several powers of 10. Economically speaking, the column still is of advantage where operational pressures above 2 mm. Hg are permissible and molecular or unobstructed path stills are of advantage in the pressure range below that figure. Distillation apparatus of the molecular and unobstructed path type are now available in sizes giving a throughput from a few grams/hour to 500 kilograms/hour.

Sommaire : Discussion de la distillation moléculaire et la distillation à parcours non retrécis, avec référence particulière au traitèment de matières à point d'ebullition élevé, mais sensibles à la temperature.

Article by R. Jaeckel *Erdöl. u Kohle* **4**, 1951 175-176

Performance of Packed Columns During Batch Fractionation 51/III

United States. The article is written in three parts (1) Mixtures for Testing Distillation Columns at Atmospheric and Reduced Pressures. (2) Effect of Reduced Pressure on Packed Columns Operating at Total Reflux. (3) Packed Column Performance When Reflux Ratio is Finite. A proper evaluation of packed column performance, if operated at reduced pressures, has hitherto been difficult for the reason that no test mixture was available which could be used at both atmospheric and reduced pressures. The properties required of a test mixture which is to be used at pressures ranging from 760 mm. to 20 mm. Hg are the following :—Its components should be obtainable in a high state of purity; its constituents should form a nearly ideal solution; it should be capable of easy and accurate analysis; its boiling point at the lowest pressure should be above room temperatures; its relative volatility should be in the range of 1.05 to 1.15. In the view of the authors, confirmed by experiments, the mixture ethylbenzene-chlorobenzene satisfies all these requirements. Another mixture recommended for use in the range of 760 mm. Hg to 300 mm. Hg is n-heptane-methylcyclohexane. In the second part of the article tests are described using both mixtures in experiments on the performance of two types of columns, (1) fitted with a fixed-type packing (spiral screen) and (2) fitted with Raschig rings. It is shown that the spiral-screen column performance is at least as good at 20 mm. Hg pressure as at atmospheric pressure up to a rate of throughput, where flooding occurs. The tests on the column packed with Raschig

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rings were less satisfactory. In the third part of the article various known methods of assessing batch distillation performance are surveyed. A new criterion is introduced which simplifies the expression of performance results, termed ' operating efficiency '. This is defined as the number of equivalent plates exerted, when the take-off is finite, divided by the number of theoretical plates which the column shows under total reflux for the same rate of throughput.

Sommaire : Cet article traite des mélanges conveyant à la vérification des colonnes de distillation aux pressions atmosphériques et réduites.

Article by J. E. Hawkins & J. A. Brent, Jr. *Industr. Engng. Chem.* **43**, Nov. 1951 2611-2621

A Simplified Construction for Vacuum Distilling Apparatus

52/III

United States. The author, an instructor, describes an all-glass distillation apparatus for use in courses on vacuum distillation technique. At the same time the still is suitable for laboratory work. Column, condenser and fractiondistributor are all blown from one piece of glass tubing. The fractions can be taken off without interrupting the operation of the still. A list is given of all components used, showing their dimensions and the material from which they are made. It is suggested to employ a motor-driven vacuum pump instead of the conventional desk aspirator. The new apparatus saves much time lost in the past on the assembly of apparatus and is foolproof in operation.

Sommaire : Construction d'un appareillage de distillation pour emploi dans les laboratoires scolaires.

Note by R. Wendland *J. Chem. Educ.* **28**, June 1951 332-333

A Modified Spinning-Band Column For Low Pressure Fractionation

53/III

Australia. It is difficult to obtain good separation of fatty acids in packed columns due to the danger of decomposition of the larger molecules resulting from the considerable pressure drop between boiler and head of the still. Spinning-band columns operated at low pressures very largely overcome these difficulties. A design of a spinning-band column is described having a length of 145 cm. and an internal diameter of 15 mm. Care has been taken to centre the rotating band accurately at intervals of 29 cm. along the axis of the column. Five rotor designs were tested. The most efficient design, now incorporated in the still, consists of a shallow S in section and is fitted with gauze soldered to the tip of the blades wiping the inner surface of the column. The efficiency of the column was tested at atmospheric pressure with a mixture of n-heptane-methylcyclohexane of approximately 80 mole % methylcyclohexane. The tests at reduced pressure were carried out with a mixture of n-hexadecanol and n-octadecanol. The influence of the speed of the spinning band was studied and it was found that the efficiency of the column increased up to a speed of 1,400 r.p.m. The low pressure drop of the column (approximately 0.4 mm. Hg) makes it possible to fractionate compounds with 30 or 32 carbon atoms without decomposition, operating in the range of 0.5 to 2.0 mm. Hg.

Sommaire : Etude de la construction de colonnes de distillation à ruban tournant, fonctionnant à basse pression, pour le fractionnement d'acides gras.

Article by K. E. Murray *J. Amer. Oil Chem. Soc.* **28**, June 1951 235-239

A Spinning-Band Column for Vacuum Fractionation of Fatty-Acid Esters

54/III

United Kingdom. Details are given of the construction and application of a spinning-band column specially designed for analytical fractionation of fatty-acid methyl esters. The column itself consists of a precision-bore Pyrex tube of 18 mm. diameter held centrally in a thick Pyrex glass sleeve. Heating is effected by nichrome ribbons wound on to the sleeve. The band consists of a 24 ga. Staybrite F.M.B. strip, 82 cm. long and 1.6 cm. wide. 12 semi-circular segments of 34 ga. stainless steel are rivetted at right angles to the band. The ordinary speed of the band is 1,400 r.p.m. The band is driven by a motor *via* a pulley drive fitted to a stainless steel rod to which the band is loosely rivetted and which is introduced into the distillation chamber through a vacuum-tight gland. The still boiler is immersed in an electrically heated oil bath. Performance tests were carried out at atmospheric and at sub-atmospheric pressures. The results of these tests are given in three tables which are reproduced below :

TABLE I

Boil-Up Rate ml./hr.	*Total Plates*	*H.E.T.P. cm.*
200	31	2.64
300	27.5	2.98
400	24.0	3.42

TABLE II

Estimated Boil-Up Rate. ml./hr.	*H.E.T.P. cm.*	*Pressure Drop mm. Butyl-phthalate*	*Pressure Drop per Theoretical Plate. mm. Hg.*
150	6.8	5-6	0.037
250	8.2	10	0.074

TABLE III

Estimated Boil-Up Rate. ml./hr.	*H.E.T.P. cm.*	*Pressure Drop per Theoretical Plate. mm. Hg.*	*Pressure mm. Hg.*
ca 200	5.7	0.034	3.0
"	4.9	0.031	1.0
"	5.7	0.036	0.5

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The values shown in Table II were obtained at 1 mm. Hg pressure and the values shown in Table III at still lower pressures. The column effects good separation of higher saturated fatty-acid esters, for example, the separation of non-hydroxylated C_{18} esters from methyl ricinoleate at an operating pressure of 0.5 mm. Hg to 0.1 mm. Hg. For the separation of unsaturated fatty-acid esters a longer column should be used.

Sommaire : Description de la construction et des caractéristiques d'une colonne de distillation à ruban tournant, conçue pour le fractionnement analytique d'esters méthyliques d'acides gras.

Article by L. J. Williamson *J. Appl. Chem.* 1, Jan. 1951 33-40

Modern Analytical Distillation of Crude Petroleum

55/III

United States. Details are given of the equipment required for standard analyses of crude oil as carried out by the California Research Corporation. The equipment essentially consists of three pieces of apparatus : (1) A spinning-band column, 0.5 inches in diameter and 3 ft. long, in which almost the entire distillation of crude oil is performed. The still operates at 1 mm. Hg pressures. (2) A simple molecular still of laboratory size. (3) An all-glass equilibrium flash vaporisation still. The equipment mentioned is used to carry out several standardised procedures, a.o., product breakdown and true boiling point analyses. The spinning-band column is based on the design by Burch, Gripp and Nathan but has been modified in certain respects to allow for routine operation by unskilled workers. The column consists of heavy-walled borosilicate glass tubing and is vacuum jacketed and silvered to ensure adiabatic operation. The walls of the vacuum jacket are covered with a heating mantle to minimise heat losses and strains during high temperature work. The band is stainless steel twisted through a spiral of 720° throughout its length. The band extends into the still pot to act as a stirrer and rotates at 3,000 r.p.m. in a direction opposing the rising action of the vapours. At the end of a low pressure distillation rotation is reversed, thus causing the band to operate as a vapour pump. The column shows an efficiency equivalent to 20 theoretical plates under the following conditions : test mixture, n-heptane and methylcyclohexane; atmospheric pressure; total reflux; boil-up rates of 2 litres/hour. The boil-up rate at 10 mm. Hg is 2 litres/hr. and at 1 mm. Hg 1 litre/hr. As a result of the experience gained with the operation of the band as a vapour pump a small still with a band in the form of an auger was developed. This still has a column 8 inches long and 1.25 inches diameter. The auger is made from ordinary wood, all other design details are similar to those of the column described previously. The auger rotates at 5,000 r.p.m. Overhead rates of 200 ml./hr. have been achieved in this still even at a pressure of 1 micron Hg.

Sommaire : La California Research Corporation décrit son installation pour l'analyse standardisée de l'huile non rectifiée.

Article by J. A. Lockwood R. L. LeTourneau R. Matteson & F. Sipos *Analyt. Chem.* 23, Oct. 1951 1398-1404

Vacuum Distillation Apparatus

56/III

United States. In existing high vacuum unobstructed-path stills the heat is applied to one side of the vaporising surface and is lost on the other, due to distillation and radiation. There is thus a heat gradiant throughout the film of distilland present on the vaporising surface. In order to heat the active surface of the distilland to the accurate distillation temperature it is necessary to apply excess heat to the vaporising surface. This involves the danger of decomposition and rapid deposition of solids on the vaporising surface. The new design proposed in this patent provides for the active distillating surface to be heated directly by means of a radiant heater so positioned that it is not in contact with the distilling vapours. Several embodiments of the invention are shown. In one design the vaporising surface is rotated and partially heated by heater elements placed underneath. The distilland spreads over the surface by centrifugal force and the undistilled residue is thrown into a stationary gutter. The rising vapours come into contact with stationary cooling baffles which are arranged in the form of annular collars and are cooled by special means. In the centre, above the annular collars forming the condenser, the radiant heater and reflector are positioned in such a manner that the heat is focussed on the vaporising surface and only a little of the heat is radiated on to the condensing baffles.

Sommaire : Description d'un alambic sous vide poussé à voie libre, où l'on traite directement à chaud le film du distillat formé sur la surface de vaporisation.

K. C. D. Hickman & Eastman Kodak Co. *U.S. Pat.* 2,537,967

A Distillation Apparatus

57/III

United States. The design of a short-path still is described which consists of a rotating condenser unit situated close to the stationary vaporiser. The condenser unit is fitted with an internal liquid-cooling system. The condenser surface is of conical shape to assist the discharge of condensate from the condenser surface. The condenser surface is larger than the evaporator surface in order to keep refluxing at a minimum and make low-pressure operation as effective as possible. The vacuum pump, if required, can be placed inside the distillation chamber. The housing of the chamber is of double-walled construction designed for the circulation of cooling liquids between the two walls.

Sommaire : Description d'un alambic à parcours raccourci qu'on peut faire fonctionner sous vide.

B. H. Thurman Kraft Foods Co. *U.S. Pat.* 2,538,540

Vacuum Distillation

58/III

United States. The patent describes a new method and apparatus for high vacuum or molecular distillation, wherein the distilland flows filmwise down a substantially vertical evaporating surface, and the condensate collected on a rotating condenser is thrown upwards and back upon the evaporating surface by centrifugal means. (*Nuclear Science Abstracts*)

Sommaire : Description d'un nouveau systeme d'alambic moleculaire.

T. I. Taylor & U.S. Atomic En. Comm. *U.S. Pat.* 2,562,153

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Greaseless Stopcock for Use at Sub-Atmospheric Pressures 59 III

See Abstract No. : 35/II

39 — MISCELLANEOUS PROCESSES — 39

Rapid Heat Processing of Fluid Foods by Steam Injection 60 III

United States. In order to improve existing methods for short-time high-temperature heat processing and concentration of fluid foods, such as fruit and vegetable juices, a new type of equipment has been developed and the results of its operation on a pilot plant scale are described. The plant consists essentially of a pre-heater, a steam injection heater supplied with clean steam, a combination evaporator and a vapour liquid separator. The two main features of the equipment are the steam injection heater and the combination evaporator. The injection heater is made from a 12 inch length of 3/8th inch i.p.s. stainless steel pipe and consists essentially of the following components : product inlet tube, heater body fitted with a thermocouple, discharge orifice and product outlet tube. The steam is admitted to the heater body tangentially. This apparatus preheats or superheats the processed material before it enters the evaporator. The latter consists of a steam jacketted tube made from stainless steel ½ inch i.p.s. and 6 ft. long. The material reaching the evaporator is concentrated by evaporative cooling at a pressure below its vapour pressure at the temperature prevailing in the injection heater. The amount of water evaporated is proportional to the heat which has to be removed in order to cool the material down to its vapour-liquid equilibrium temperature in the separator. The combination evaporator and steam injection heater are operated as continuous processing units. For the pasteurisation of milk, raw milk was processed in the plant, *i.e.* it was heated to 245°F in the injection heater and cooled evaporatively to 80°F, the whole process not taking longer than 0.7 seconds. The raw milk was concentrated from 11.4% to 26.0% solids in a single pass through the combination evaporator with the injection heater operating at 244°F and the evaporator kept under low pressure. The enzyme phosphatase in raw milk was found to be inactivated by heating the milk to 185°F and cooling evaporatively to 95°F in a total time of 0.4 seconds. Results with other food materials are also given.

Article by A. H. Brown M. E. Lazar-T. Wasserman G. S. Smith & W. M. Cole *Industr. Engng. Chem.* **43**, Dec. 1951 2949-2954

Sommaire : Compte rendu des résultats obtenus par une installation d'essai d'un nouveau procédé de chauffage rapide, par injection de vapeur, de produits alimentaires fluides.

Inert Gas : Safeguard of Quality 61/II

United States. Nitrogen processing and packaging in the food industry is not new but its importance is still growing. Nitrogen gas can be used in processing and packaging of foods like edible oils, margarine, coffee, dried activated yeast, nut meats, sandwich meats, bacon, sausages, dehydrated potatoes, etc. The proper protection of food products depends essentially on the effectiveness with which oxygen can be kept out or removed from the container. The atmospheric air consists of about 1/5th of oxygen, the remainder is mainly nitrogen. This means that breaking back a vacuum with nitrogen does not reduce the amount of oxygen present and it is important therefore to use nitrogen of extreme purity only. If the product is unstable and persistently releases dissolved oxygen, packaging in vacuum or providing nitrogen head space is not the complete solution. For example, a product contains about 0.6 cm^3 of dissolved oxygen in every hundred cm^3 of liquid and the container is designed to allow for a head space of 10%. If packed with air in the head space the total oxygen content will be about 2.95 cm^3 per 100 cm^3 of liquid. Only by purging the head space with nitrogen or by nitrogen stripping can this figure be reduced to 0.8 cm^3. It is important to have accurate knowledge of the rate at which oxygen diffuses through a film used for packaging. Even if the film is free of pin holes and has good sealing properties oxygen can be transferred by diffusion due to the difference between the partial pressure of oxygen inside the package and the surrounding atmosphere. A product packed in vacuum may appear to be gas-tight but unless the film possesses an inherently low oxygen permeability, product deterioration by chemical absorption of diffused oxygen can occur without apparent change of pressure.

Article by T. W. Eselgroth *Food Engng.* **23**, Dec. 1951 72-75, 153 & 155

Sommaire : Discussion des diverses formes d'application d'azote dans l'empaquetage des produits alimentaires.

Frozen Concentrated Apple Juice 62/III

See Abstract No. : 31/III

Costs and Methods for Pie-Stock Apples 63/III

United States. The cost of supply of pie-stock apples to a distant market is influenced mainly by two considerations : weight and volume of the packaged product and the storage and transport conditions required. The Western Regional Research Laboratory have compiled cost estimates to provide an economic foundation on which to base laboratory work on improved processes. The Pacific States are growing more apples than can be consumed locally and are compelled to sell their surplus in Eastern markets. The article gives the relative costs of supplying Eastern markets with Western apples processed by various methods. The following processes are taken into account : (1) Dried. (2) Vacuum Dried. (3) Dehydrocanned. (4) Canned. (5) Dehydrofrozen.

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(6) Frozen, no sugar. (7) Frozen, syrup filled, sugar 1 : 20. (8) Frozen, sugar 1 : 5 . (9) Frozen, syrup filled, sugar 1 : 5. The processes nos. 3, 5 and 7 are still in the experimental stage. Flow sheets are given of all processes. Tables are added detailing the production and distribution cost for each process. One of these tables is reproduced below in abbreviated form :

	Dried	*Vacuum Dried*	*Canned*	*Frozen No Sugar*	*Frozen Sugar 1 : 5*	*Fresh Washington Apples*
Costs per 100 lb. of Fresh Apples						
Raw materials	$1.50	$1.50	$1.50	$1.50	$2.57	$1.50
Processing other than packaging	1.32	1.66	1.18	1.29	1.33	
Packaging	.17	.22	1.31	1.19	1.19	2.75
Selling, brokerage and profit	.53	.59	.71	.70	.90	
Selling Price, F.O.B. Processor	3.52	3.98	4.70	4.68	5.99	4.25
Storage, 6 mo	.04	.09	.23	1.09	1.29	—
Transportation, West Coast to Chicago ...	.27	.25	1.07	1.50	1.77	1.66
Cost to Distributor	$3.83	$4.32	$6.00	$7.27	$9.05	$5.91

Sommaire : On reproduit ici une étude originellement effectuée par les Laboratoires de Recherches Régionales de l'Ouest des Etats-Unis (U.S.A. Western Regional Research Laboratory) et qui indique les coûts relatifs à le fourniture aux marchés de l'Est des Etats-Unis de pommes oultivées à l'Ouest et traitées par diverses méthodes de séchage sous vide.

Article by V. F. Kaufman *Food. Engng.* **23**, Dec. 1951 97-105

Production of Small Apertures by an Evaporation Technique

64/III

United Kingdom. Two methods are described for the production of small aperatures (approximately 3 microns diameter) in foil of a few thousand Å thickness. The first method is essentially a shadow casting technique providing for a metal layer to be deposited about an oil drop sprayed on to a glass surface. This method proved difficult and slow. The second method was more successful. A polished needle rests with its point on a stripping layer applied to a clean glass surface. The metal layer around the needle is deposited by evaporation from a source of circular shape, following which the needle is withdrawn. The second method lends itself to the mass production of apertures.

Sommaire : Deux méthodes pour percer des petits trous (diamétre approximatif 3 microns) dans du feuillard de quelques milliers d'Å d'épaisseur sont décrites.

Letter by A. S. Baxter *Vacuum* 1, April 1951 115-117

A Liquid Hydrogen Target

65/III

United States. Investigating mesons produced by X-rays from the Berkeley synchrotron it was desired to bombard hydrogen. Liquid hydrogen was chosen as a target. Details of the target construction are given in the article. It essentially consisted of a flask containing the liquid hydrogen, a refrigerated shield surrounding the flask, a vacuum jacket for thermal insulation and a liquid level monitoring system. The hydrogen flask was made from 2-inch diameter tubing and mounted in a position co-axial to the path of the X-ray beam. The material was stainless steel. The refrigerated radiation shield consisted of a nitrogen-filled tank formed from two co-axial stainless steel cylinders and was constructed in such a manner that the target itself was entirely surrounded by a surface kept at the temperature of liquid nitrogen. The vacuum jacket was evacuated to a pressure of 10^{-6}mm. Hg, a pressure lower than necessary to eliminate thermal conduction in gas, but extremely useful as an efficient check on the vacuum tightness of the whole system. A conventional diffusion pump was used. Charging was effected in the following way : after evacuation of the vacuum jacket the charging system was filled with helium gas to a positive pressure of 5 psi and the liquid nitrogen shield was filled. A few hours later the Dewar vessel was connected to the charging system and a transfer tube inserted to convey the hydrogen to the target flask. The connection to the gas exhaust of the target was then opened and the helium forced into the Dewar vessel driving the liquid hydrogen through the transfer tube into the hydrogen flask. When the flask was filled the header of the Dewar vessel was vented through a by-pass line into the main exhaust system.

Sommaire : Une anticathode d'hydrogène liquide est décrite, laquelle fut utilisée dans l'étude de mesons produits par rayons-X à partir du cyclotron de Berkeley.

Article by L. Cook *Rev. Sci. Instrum.* **22**, Dec. 1951 1006-1008

Heating In Vacuo by an External Radiation Source

66/III

United Kingdom. In the course of experiments the need arose of heating an object of small dimensions situated in an evacuated vessel. In this particular case the dielectric heating normally applied could not be used. Therefore an attempt was made to apply heat by radiation. A tungsten filament lamp of 750 watt was placed at one focus of an ellipsoidal reflector and the object to be heated at the other. The experiment was successful. The object in the evacuated vessel was heated to a temperature of 1,300°K. Various applications of the device are suggested but there may be more than those mentioned by the authors.

Sommaire : Un dispositif est décrit pour le charffage d'un petit object dans un recipient évacué, par rayonnement.

Letter by A. Leemans & R. Kompfner *Vacuum* 1, July 1951 203-204

Vacuum-Powder Insulation for Low Temperatures

67/III

See Abstract No. : 23/I

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40 — GASES AND VAPOURS — 40

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See Abstract No. : 38/I

41 — FREEZE DRYING — 41

The Theoretical Factors of Vacuum Drying 12/IV
See Abstract No. : 28/III

A Review of Laboratory Freeze Drying with Particular Reference to Viruses 13/IV

United Kingdom. The following aspects of freeze drying are briefly considered, firstly, the physical principles; secondly, the objectives of this method of desiccation; thirdly, application of the method to : (1) the stabilisation of enzymes, (2) the preservation of body fluids and of media for bacterial and tissue cultivation, (3) the preservation of bacteria, (4) the preservation of plant and animal viruses, and (5) the preservation of tumour-producing

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viruses with special reference to the claims of Gye and Craigie, and to the work of the author and his collaborators on the preservation of fowl tumour viruses. Lastly, a few of the technical difficulties, and problems, are considered which remain to be solved.

Sommaire : On considère plusieurs aspects de la dessication à froid sous vide avec référence au traveaux de l'auteur et ses collaborateurs concernant la conservation des virus.

Article by R. J. C. Harris *Vacuum* 1, Jan. 1951 11-22

Freeze Drying—Vacuum Sublimation 14/IV

United Kingdom. A short account is given of the principles involved in the dehydration of heat sensitive materials by sublimation from the frozen state. References are made to drying rates and important design features of commercial apparatus. (*Author*)

Sommaire : Bref compte-rendu sur les principes de la séchage de matières sensibles à la chaleur par sublimation à partir de l'état congelé.

Article by L. G. Beckett *J. Sci. Instrum.* Suppl. 1, 1951 66-68

Symposium on Freezing and Drying 15/IV

United Kingdom. A report is given on the proceedings of the Symposium on Freezing and Drying organised by the Institute of Biology and held in London on June 29th and 30th 1951. Added to this report are abstracts of all lectures presented to the conference, the titles and authors of which are listed below :

Some Applications of Freezing and Drying in Cytochemistry.
Author : *L. G. E. Bell.*

The Influence of the Suspending Fluid on the Survival of Bacteria After Drying.
Author : *R. M. Fry.*

A Difficulty in the Quantitative Freeze Drying of Certain Materials.
Author : *W. Smith.*

Effects of Freezing and Drying Compared with Common Fixation Procedures.
Author : *B. Sylven.*

The Freeze Drying of Living Virus Vaccines for Veterinary Use.
Author : *R. Daubney.*

Contributions on Problems Encountered in Drying Viruses, Vaccines and Antisera by Sublimation.
Author : *I. A. Galloway.*

Preservation of Spermatozoa, Red Blood Cells and Endocrine Tissue at Low Temperatures.
Author : *A. S. Parkes.*

Aspects of the Design of Freeze Drying Apparatus.
Authors : *A. S. D. Barrett and L. G. Beckett.*

Survival of Cells, Tissues and Organisms after Ultra-Rapid Freezing.
Author : *B. J. Luyet.*

Freeze Drying of Foodstuffs.
Author : *R. Gane.*

Some Recent Experiments in Fixation by Freezing and Drying.
Author : *I. Gersh.*

Infection and Drying Techniques.
Author : *S. T. Cowan.*

Freeze Drying of Tissues for Cell Analysis by Light and Electron Microscopy.
Author : *F. Sjostrand.*

Some of the Factors Affecting the Viability of Bacterial Cultures Subjected to the Freeze Drying Process.
Author : *H. Proom.*

The Preservation of Vaccinia Virus by Freeze Drying.
Author : *L. H. Collier.*

Freeze Drying of Tumour Tissues.
Authors : *R. D. Passey and L. Dmochowski.*

Freeze Drying of Antibiotics on a Commercial Scale.
Author : *J. H. Singer.*

The Viability of Mammalian Skin After Freezing, Thawing and Freeze Drying.
Authors : *R. E. Billingham and P. B. Medawar.*

Large Scale Freeze Drying as Currently Carried out in the Western Hemisphere.
Author : *E. W. Flosdorf.*

Sommaire : On donne des extraits de toutes les conférences publiées à l'occastion du Congrès de la Congélation et du Séchage qui s'est tenu à Londres sous les auspices de l'Institut de Biologie, du 29 au 30 Juin 1951.

Report by R. J. C. Harris *Vacuum* 1, Oct. 1951 294-299

45 — ELECTRONICS — 45

An Introduction to High Vacua in Nuclear Physics 16/IV

See Abstract No. : 21/I

A New Type of High Intensity Ion Source 17/IV

France. The ionisation source is of annular shape and is inserted in the annular gap of a magnet. The resulting beam of ions is of tubular shape, a form particularly favourable from the point of view of dispersion effects caused by space charge. High intensity may be obtained. (*Nuclear Science Abstracts*)

Sommaire : Description d'un appareil à source d'ionisation de forme annulaire que l'on insère dans le champ annulaire d'un aimant.

Letter by J. Sommeria *J. Phys. Radium* 12, April 1951 563-564

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Noble Gas Hot-Cathode Diodes with Negative Arc Drop

18/IV

United States. Research work carried out previously led to the assumption that a negative arc drop could be obtained in hot-cathode diodes filled with a noble gas if the work function of the anode is lowered and that of the cathode increased at the same time. The diode used in the experiment carried an indirectly heated tantalum cathode serving as a equi-potential high work-function cathode. The work-function of the anode was lowered by the deposition of barium on its surface. As a result a negative voltage drop up to 0.8 volts developed at approximately 0.5 amps. The tube was filled with xenon at a pressure of approximately 0.1 mm. Hg. The tube worked as an e.m.f. where part of the heating energy of the cathode was transformed directly into electrical energy. Measurements proved that the discharge mechanism is the same in this case as in the case of the positive arc drop investigated previously, only the current-voltage characteristics had shifted so that a negative voltage drop appeared.

Sommaire : L'auteur décrit une expérience qui démontre les conditions sous lesquelles l'on peut obtenir une chute de l'arc négative.

Letter by G. Medicus and G. Wehner *J. Appl. Phys.* **22**, Nov. 1951 1389

Photo-Electric Cathodes of the Lithium-Antimony Type

19/IV

See Abstract No. : 30/I

Photo-Conductivity and Some Other Electrical Properties of Thorium in an Evacuated Space

20/IV

France. The authors refer to comprehensive research work, they have carried out in the past, on the uses of thorium as a material for thermionic cathodes and proceed to give details of the experimental tubes they employed for the measurement of electrical conductivity properties of thorium. Finally they give details of the procedure employed to measure the resistance and thermo-electric e.m.f.

Sommaire : Discussion des propriétés et du comportement du thorium employé dans les récipient evacués.

Article by G. Mesnard and R. Uzan *Le Vide* **6**, July-Sept. 1951 1052-1062

Thoria as a Cathode Emitter

21/IV

United States. Thoria cathodes have been recommended for application in electron tubes in cases where barium-strontium oxide coatings show no satisfactory service life. Thoria cathodes require higher temperatures for their operation than barium-strontium oxide cathodes and therefore consumes more electrical energy. The author investigated whether the advantages offered by thoria cathodes justify their use in spite of their high consumption. He found the thoria is more refractory and its activation less easily disturbed. An activated thoria cathode gives a relatively high stable emission in the pressure region of 10^{-5} to 10^{-4}mm. Hg. Its service life is limited by two factors : (1) the rate at which evaporation takes place and (2) the rate at which disintegration of the material proceeds on account of the passage of current. At 1,700°C, true temperature, thoria evaporated at a rate of 1 mil. thickness in 100 hours at a current density of 200 ma./cm^2.

Sommaire : Discussion des propriétés et de la performance des cathodes de thorine dans les tubes électroniques.

Article by W. E. Danforth *J. Franklin Inst.* **25**, May, 1951 515-520

Cathode Coatings

22/IV

United States. The emission of thermionic type cathodes is increased 2½ times by coating with an adherent mass of fine interlocking crystals in close thermal and electrical contact with the cathode metal core and with each other. A mixture of $BaCO_3$ and $SrCO_3$ containing 25% by weight $BaO_2H_2O_2$, amyl acetate, and nitro cellulose lacquer is applied, and air dried; the apparatus is assembled, sealed, evacuated, heated to 450° to fuse the perioxide (some carbonates are thus dissolved in the perioxide, some gas evolved), and finally heated to 800° to give a coating of BaO and SrO. (*Chemical Abstracts*)

Sommaire : Un procédé breveté de fabrication de cathode d'oxyde de barium.

C. W. Becker & Raytheon Mfg. Co. *U.S. Patent* 2,559,530

The Effect of Ion Bombardment on the Emission from Oxide-Coated Cathodes

23/IV

Canada. The preliminary results are given of an experimental study concerned with the changes in emission caused by the bombardment of cathode surfaces by positive ions formed in normal tube operations. Three cases are considered :—operation under temperature limited conditions, operation under space-charge limited conditions and the effects of emission density. Oxide cathodes operated under temperature limited conditions are the most sensitive to poisoning. Double triodes with separate cathodes were used for the experiment to ensure that the pressure of residual gases would be identical in the two tubes tested under different conditions. Five tubes of the double triode type were diode-connected and five were triode-connected. The triode-connected batch of tubes was subjected to ion bombardment, the diode-connected batch was not. Keeping the initial anode current substantially the same for both batches and running the tubes for about 20 hours showed that the diode emission remained approximately constant, whilst the triode emission decreased rapidly at first and finally approached a steady value. Reversing the connections of the two batches resulted in the first batch showing a similar decay as in the case of the previous experiment and the second batch showing a recovery to about 75% of the initial value of emission. Under space-charge limited conditions similar experiments were carried out operating the cathode at approximately 1,050°K. The emission from the diode-

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connected batch was fairly constant for about 6,000 hours whereas the triode-connected batch showed a decay settling at a steady emission value after about 4,000 hours. Investigating the effects of increasing the emission density it was found that the cathode life is not diminished, even if the emission density is appreciably increased, provided no ionisation occurs in the tube.

Sommaire : L'auteur rend compte des résultats préliminaires d'une étude expérimentale des modifications de l'émission, causées par le bombardement de la surface de la cathode par des ions positifs formés en fonctionnement normal de la tube.

Article by P. A. Redhead *Canad. J Phys.* **29**, Sept. 1951 362-369

Activation of High Vacuum Oxide Cathode Valves

24/IV

United Kingdom. The article discusses various aspects of the activation of high vacuum oxide cathode valves. The three current theories of activation—chemical reduction, electrolysis and thermo-dynamic—are considered and discussed on the basis of the author's own laboratory experience. None of the theories is considered to give at present an adequate explanation of the high level of initial activation now common in oxide cathode valves.

Sommaire : L'article discute differents aspects de l'activation de tubes à haut vide à cathode d'oxydes.

Article by G. H. Metson *Vacuum* **1**, Oct. 1951 283-293

Vacuum Techniques—Its Application to Radio and Electronics

25/IV

See Abstract No. : 8/I

Method of Preparing Skiatronic Screens

26/IV

See Abstract No. : 17/III

Research on Electronic Valves Assisted by Radio-Active Materials

27/IV

France. The authors made use of radio-active isotopes for the study of phenomena in electronic valves which it is difficult to explore by conventional methods. For instance, radio-active barium used as a getter can yield information on the distribution of the getter deposits on the walls of the valve. Oxide cathodes with two layers, one of which is radio-active, can be employed to trace the migration of barium during the service life of the valve. Finally, the authors found that cathodes made from a nickel-cobalt alloy which has been rendered radio-active by bombardment with neutrons showed an emissivity considerably lower than that of identical cathodes not rendered radio-active, when used in diodes under the same conditions.

Sommaire : On donne des examples de l'utilisation des isotopies radio-actives pour l'examen de certains phénomènes en tubes électroniques.

Article by J. Debiesse & G. Neyret *Le Vide* **6**, Nov. 1951 1098-1102

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Analyt. Chem.	Analytical Chemistry, American Chemical Society, 1155, Sixteenth Street, N.W., Washington 6, D.C., U.S.A.
Appl Sci. Res.	Applied Scientific Research, Martinus Nijhoff, The Hague, Holland.
Arch. Tech. Messen	Archiv für Technisches Messen, R. Oldenbourg Verlag, Lotzbeckstrasse 2 b, Müchen, Germany.
Bell. Lab. Rec.	Bell Laboratories Record, Bell Telephone Laboratories Inc., 463, West Street, New York 14, N.Y., U.S.A.
B.S.I.R.A. Bulletin	Bulletin of the British Scientific Instrument Research Association, British Scientific Instrument Research Association, Information Department, 'Sira,' Southill, Elmstead Woods, Chislehurst, Kent, England.
Bull. Classe Sci.	Bulletin de la Classe des Sciences, Academie Royale de Belgique, Palais des Academies, Rue Ducale 1, Bruxelles, Belgium.
Canad. J. Phys.	Canadian Journal of Physics, The National Research Council, Ottawa, Canada.
Canad. J. Technol.	Canadian Journal of Technology, The National Research Council, Ottawa, Canada.
Chemical Abstracts	Chemical Abstracts, American Chemical Society, c/o Ohio State University, Columbus 10, Ohio, U.S.A.
Chem. Engng.	Chemical Engineering, McGraw-Hill Publishing Co. Inc., 330, W. 42nd Street, New York 36, N.Y., U.S.A.
Chem. & Industr.	Chemistry and Industry, Society of Chemical Industry, 56, Victoria Street, London, S.W.1., England.
C. R. Acad. Sci., Paris	Comptes Rendus des Séances de L'Academie des Sciences, Messrs. Gauthier-Villar, Quai des Grands-Augustine 55, Paris, France.
Erdöl u. Kohle	Erdöl und Kohle, Industrieverlag Hernhaussen Komm. Gès. Alsterufer 4/5, Hamburg 36, Germany.
Food Engng.	Food Engineering, McGraw-Hill Publishing Co. Inc., 330, W. 42nd Street, New York 36, N.Y., U.S.A.
Gen. Elect. Rev.	General Electrical Review, General Electric Co., 1, River Road, Schenectady 5, N.Y., U.S.A.
Industr. Engng. Chem.	Industrial and Engineering Chemistry, American Chemical Society, 1155, Sixteenth Street, N.W., Washington 6, D.C., U.S.A.
J. Amer. Ceramic Soc.	Journal of the American Ceramic Society, American Ceramic Society, 2525, N. High Street, Columbus 2, Ohio, U.S.A.
J. Amer. Oil Chem. Soc.	Journal of the American Oil Chemists Society, The American Oil Chemists' Society, 35, E. Wacker Drive, Chicago 1, Illinois, U.S.A.
J. Appl. Chem.	Journal of Applied Chemistry, Society of Chemical Industry, 56, Victoria Street, London, S.W.1, England.
J. Appl. Phys.	Journal of Applied Physics, American Institute of Physics, 57, E. 55th Street, New York 22, N.Y., U.S.A.
J. Brit. I.R.E.	Journal of the British Institution of Radio Engineers, British Institution of Radio Engineers, 9, Bedford Square, London, W.C.1., England.
J. Chem. Educ.	Journal of Chemical Education, Div. of Chemical Education of the American Chemical Society, Scripps Institution, La Jolla, California, U.S.A.
J. Chem. Soc.	Journal of the Chemical Society, The Chemical Society, Burlington House, Piccadilly, London, W.1, England.
J. Electrochem. Soc.	Journal of the Electrochemical Society, The Electrochemical Society, 235, W. 102nd Street, New York 25, N.Y., U.S.A.
J. Franklin Inst.	Journal of the Franklin Institute, The Franklin Institute of Pennsylvania, Prince and Lemon Streets, Lancaster, Pa., U.S.A.
J. Opt. Soc. Amer.	Journal of the Optical Society of America, American Institute of Physics, 57, East 55th Street, New York 22, N.Y., U.S.A.
J. Phys. Radium	Le Journal de Physique et le Radium, La Societe Francaise de Physique, 10, rue Vauquelin, Paris (Ve), France.
J. Sci. Food Agric.	Journal of the Science of Food and Agriculture, Society of Chemical Industry, 56, Victoria Street, London, S.W.1, England.

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J. Sci. Instrum.	Journal Scientific Instruments, Institute of Physics, 47, Belgrave Square, London, S.W.1, England.
Leather & Shoes	Leather and Shoes, The Rumpf Publishing Co., 300, W. Adams Street, Chicago 6, Illinois, U.S.A.
Mach. Design	Machine Design, The Penton Publishing Co., Penton Buildings, Cleveland 13, Ohio, U.S.A.
Metal Finish.	Metal Finishing, Finishing Publications Inc., 11, West 42nd Street, New York 18, N.Y., U.S.A.
Metal Prog.	Metal Progress American Society of Metals, 7301, Euclid Avenue, Cleveland, 3, Ohio, U.S.A.
Metal Treatment	Metal Treatment, Industrial Newspapers Ltd., 49, Wellington Street, Strand, London, W.C.2, England.
Nature	Nature, Macmillan & Co. Ltd., St. Martin's Street, London, W.C.2, England.
Nuclear Science Abstr.	Nuclear Science Abstracts, United States Atomic Energy Commission, Office of Technical Services, Department of Commerce, Washington 25, D.C., U.S.A.
P.D.A. Journal	P.D.A. Journal, Photographic Dealers Association, P.D.A. House, 46, Bloomsbury Street, London, W.C.1, England.
Physica	Physica, Martinus Nijhoff, The Hague, Holland.
Proc.Phys. Soc.	Proceedings of the Physical Society, The Physical Society, 1, Lowther Gardens, Prince Consort Road, London, S.W.7, England.
Proc. Roy. Soc.	Proceedings of the Royal Society, The Royal Society, Burlington House, Piccadilly, London, W.1, England.
Prod. Finish	Product Finishing, Sawell Publication Ltd., 4, Ludgate Circus, London, E.C.4, England.
Rev. Sci. Instrum.	Review of Scientific Instruments, American Institute of Physics, 57, E. 55th Street, New York 22, N.Y., U.S.A.
Science	Science, American Association for the Advancement of Science, 1515, Massachusetts Avenue, N.W., Washington 5, D.C., U.S.A.
Science Abstracts	Science Abstracts, Institution of Electrical Engineers, Savoy Place, London, W.C.2, England.
The Times (Industr.Suppl.)	The Times Industrial Supplement, The Times Publishing Co., Printing House Square, London, E.C.4, England.
Trans. A.S.M.E.	Transactions A.S.M.E., American Society of Mechanical Engineers, 29, West 39th Street, New York 18, N.Y., U.S.A.
Trans Faraday Soc.	Transactions of the Faraday Society, The Faraday Society, Aberdeen University Press Ltd., 6, Upper Kirkgate, Aberdeen, Scotland.
Le Vide	Le Vide, Societe Francaise des Ingenieurs des Techniciens du Vide, 44, Rue de Rennes, Paris (VIe.), France.
Z. Naturforsch.	Zeitschrift für Naturforschung, Verlag der Zeits. für Naturforsch., Mathildenstrasse 29, Tübingen, Germany.

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